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(21) International Application Number: PCT/US92/10296 (22) International Filing Date: 25 November 1992 (25.11.92) (30) Priority data: 796,729 25 November 1991 (25.11.91) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Dr., Baytown, TX 77520 (US). (72) Inventor: TURNER, Howard, William ; 4318 Misty Heath- er Court, Houston, TX 77059 (US). (74) Agents: SPEIRING, M. Susan; Exxon Chemical Com- pany, P.O. Box 5200, Baytown, TX 77522 (US) et al.		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: POLYONIC TRANSITION METAL CATALYST COMPOSITION (57) Abstract Improved ionically activated transition metal catalyst compositions which are useful in the polymerization of olefins comprise a transition metal cationic component associated with and stabilized by a polyanionic moiety comprising a plurality of metal or metalloid - containing non-coordinating anionic groups pendant from and chemically bonded to a core component.		

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Title: POLYIONIC TRANSITION METAL CATALYST
COMPOSITION

FIELD OF THE INVENTION

This invention relates to polyionic catalyst
5 compositions and their use to polymerize olefins,
diolefins and/or acetylenically unsaturated monomers to
homopolymer and copolymer products.

BACKGROUND OF THE INVENTION

10 Ziegler-Natta (Z-N) and metallocene-alumoxane type
catalyst systems for the polymerization of olefins are
well known in the art. Recently a new, ionic pair type
of catalyst has been developed which yields polymers of
improved properties compared to those made with
15 conventional type catalysts systems. Among the various
publications regarding ionic catalysts, the first to
describe this new system was Turner, et al. in EPA
277,003 and 277,004. EPA 277,003 and EPA 277,004
disclose new cyclopentadienyl based catalyst systems
20 comprising an ionic compound wherein the
cyclopentadienyl transition metal component or
metallocene is reacted with an activator comprising an
anion and a cation; the cation being one which is
reactable with a non-cyclopentadienyl ligand of the
25 cyclopentadienyl moiety to yield as the reaction
product a neutral ligand derivative, and a cationic
metallocene species to which the anion of the activator
compound is essentially non-coordinating. EPA 277,003
describes an anion component which comprises a
30 plurality of boron atoms while EPA 277,004 describes an
anion species which is a single coordination complex
shielding a central charge-bearing metal or metalloid
atom.

These ionic complexes can optionally be placed on
35 a support as described in PCT WO91/09882. In
accordance with WO 91/09882, the ionic catalyst is

physi-sorbed onto an inert carrier which has been previously dehydrated and treated with an alkyl aluminum solution. The ionic catalyst is not covalently bonded onto the support carrier and is
5 extractable or desorbable by solvents.

While improvements in catalyst activity and processing were observed with both the homogeneous and heterogeneous ionic catalyst described above, further improvements are sought for the catalyst system through
10 anion effects as well as to address the issue of catalyst desorption found when heterogeneous catalyst are used. The publications referred to contain no teachings or suggestions as to the advantages which may derive from having a plurality of non-coordinating
15 anion species chemically e.g. covalently bonded to a core component.

SUMMARY OF THE INVENTION

20 According to the present invention there is provided a polyanionic moiety comprising a plurality of metal or metalloid atom - containing non-coordinating anionic groups pendant from and chemically bonded to a core component. The pendant groups may be chemically
25 e.g., covalently bonded to the core directly or via a bridging atom or group.

In one aspect of the invention the defined polyanionic moiety is derived from an intermediate compound in which the metal or metalloid element of the
30 non-coordinating anionic groups is chemically bonded to a reactive radical containing at least one reactive functional group. The radical is chemically reactable with the pre-existing core component, or is polymerizable with other such intermediate compounds
35 and optionally other comonomer to form the core component. In this latter case the polymeric core will carry the plurality of pendant non-coordinating anionic

groups because at least one such group is bonded to each polymer precursor (intermediate compound) monomer molecule.

In use of the invention, the polyanionic moiety may exist in combination with balancing cationic species. Thus another aspect of the invention provides a polyanionic activator composition comprising the defined polyanionic moiety and a plurality of cations which balance the charge of the non-coordinating anionic groups. The balancing cationic species may be catalytic with regard to olefin polymerization. Thus yet another aspect of the invention provides an activated catalyst composition comprising the defined polyanionic moiety, a plurality of the pendant non-coordinating anionic groups of which are in non-coordinating association with a plurality of cationic transition metal components derived from one or more ligand stabilized transition metal compounds.

The invention further provides a method of producing the defined activated catalyst composition which comprises contacting (i) a transition metal compound having at least one leaving group ligand, for example a ligand which is hydrolyzable with water, and (ii) the defined polyanionic activator composition for a time and under conditions sufficient to allow charge balancing cations of (ii) to react with the leaving group ligands of (i). Such reaction removes the leaving ligand from the transition metal compound as a reaction product with the charge balancing cations of the activator composition. What remains is a plurality of catalytically active cationic transition metal components each in non-coordinating association with a pendant anionic group of the polyanionic moiety.

It is with regard to the above mentioned catalytic cationic transition metal components that the anionic groups of the polyanionic moiety are said to be "non-coordinating". Thus the term "non-coordinating" as

applied to the pendant anionic groups of the defined polyanionic moiety means an anionic group which either does not coordinate to the cation or which is only weakly coordinated to the cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base such as ethylene monomer molecule. More specifically, in the activated catalyst compositions of this invention "non-coordinating" means an anionic group which when functioning as a stabilizing anion in the catalyst composition of this invention does not transfer an anionic substituent or fragment thereof to the catalytic cation so as to form a neutral inactive transition metal product (such as a four coordinate "catalyst" metal compound in the case where the catalyst is a metallocene) and a neutral metal or metalloid by product. The non-coordinating anionic groups are non-coordinating by virtue of their bulk. Thus they are "bulky", i.e., too large in size to fit within the coordination sphere of the transition metal cation and thus cannot form strong covalent bonds to the metal center. Such terms are further discussed hereinafter and in EP-A-277004.

Thus, this invention relates to new polyanionic non-coordinating anions or activator moieties comprising a plurality of metal or metalloid atom - containing non-coordinating anionic groups pendant from and chemically bonded to a core component, which can be used to prepare a wide variety of new ionic catalyst compositions. The invention provides polyanionic non-coordinating anions and methods of preparing such compositions. The polyanionic compositions of this invention have a negative charge greater than -1 and range in size from molecular discrete dianions to macroscopic polyanionic particles or objects. This invention further provides new ionic catalyst compositions and methods of preparing such materials from the polyanionic compositions of this invention.

In one application of this invention the polyanionic activators are used to prepare a catalyst system of enhanced performance. Such enhanced performance resides in the ability to immobilize the catalyst on a catalyst support. For industrial processes where a heterogeneous catalyst is preferred, this invention provides a method of chemically binding the cationic catalyst to the supporting material thus circumventing problems associated with catalyst desorption. The heterogeneous catalyst of this invention can be used in a wide variety of commercial process including gas phase, slurry or fixed bed reactors. In a specific case, the invention provides ionically activated transition metal catalyst compositions which are useful in the polymerization of olefins, diolefins and/or acetylenically unsaturated monomers. This invention further provides methods of preparing such catalyst compositions from polyanionic activators. When exposed to unsaturated monomers, the polymerization catalysts of this invention yield a wide variety of homo or copolymers having variable molecular weight, molecular weight distribution, and comonomer content.

The polyionic catalyst polymerization compositions are prepared by reacting a transition metal catalyst precursor ZX with a polyionic ion-exchange activator compound $[Ct^{C+}]_{y'}[(NCA^{b-})_yT]^{by-}$ to form a neutral by-product CtX and the active polyionic catalyst system $[Z^+]_{by}[(NCA^{b-})_yT]^{by-}$, wherein Z is a ligand stabilized transition metal compound, Ct^{C+} is a cation which balances charge and can be designed to react with the leaving group X which is bonded to Z , y' is the number of Ct^{C+} cations, $[(NCA^{b-})_yT]^{by-}$ is a polyanionic non-coordinating counter ion comprised of pendant non-coordinating anions (NCA) bonded to, as T , a core atom, a core molecule, a core polymer or a core network such as silica (e.g. particles) or metal oxide surface of a metal substrate, b is the charge on the non-

coordinating anion and y is an integer greater than or equal to 2. Similar procedures can be used to generate polyionic catalysts having an active site with a cationic charge greater than 1, represented by Zn^{+n} where n is an interger greater than 1. The preferred ligand stabilized transition metal components include high oxidation state Group-IV metal alkyl or hydride complexes having between 0 and 2 covalently-bound cyclopentadienyl ligands.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram which illustrates three of the most preferred synthons (1,2 and 3) and the manner by which they may be utilized to prepare derivative synthons (4, 5 and 6) and polyionic activator compositions (A-F).

Fig. 2 depicts the structure of a polyanionic silicate activator composition which can be produced in accordance with this invention.

Fig. 3 is a silica particle which can be prepared to have a polyanionic activating skin in accordance with this invention.

Fig. 4 illustrates one method of preparing polyionic activator compositions by reaction with a preformed polyionic core.

Fig. 5 illustrates a method for producing a variety of microporous polystyrene polyionic activator compositions.

Fig. 6 illustrates an anionic polymerization technique for preparing a cross-linked polystyrene with pendant living lithium polystyrene groups.

Fig. 7 illustrates how linear and cross-linked lithiated polymers can be prepared using divinylbenzene and an anionic initiator.

5

Fig. 8 illustrates a method for preparing a polyanionic composition from a surface modified glass, silica or metal substrate.

10 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Discrete catalyst cations having a variety of end uses are well known in the art. These include: hydrogenations catalysts such as $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$,
15 and $[\text{Rh}(\text{diphos})]^+$, olefin dimerization catalysts such as $[\text{Ni}(\text{L})_4\text{H}]^+$, methylacrylate dimerization catalysts such as $[\text{CpRh}(\text{L})(\text{alkyl})]^+$, late transition metal olefin polymerization catalysts such as $[\text{CpCo}(\text{L})(\text{alkyl})]^+$, as well as early transition metal olefin polymerization
20 catalysts such as $[\text{ACpZr}(\text{alkyl})]^+$, and $[\text{Me}_2\text{Si}(\text{Cp})(\text{NR})\text{Zr}(\text{alkyl})]^+$. In the foregoing, L represents a neutral Lewis basic ligand such as phosphine; diphos is a chelating phosphine; Cp is a substituted or unsubstituted cyclopentadienyl ligand;
25 ACp represents two substituted or unsubstituted cyclopentadienyl ligands which may be bridged or unbridged, and may be the same or different; and R represents a hydrocarbyl substituent. This invention provides new activator compositions comprising
30 polyanionic non-coordinating anionic moieties which can be used to improve the catalytic properties of catalyst cations such as those listed above.

As used herein, the recitation "compatible noncoordinating anion" means an anion which either does
35 not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis

base. The recitation "compatible noncoordinating anion" specifically refers to an anion which when functioning as a stabilizing anion in the catalyst system of this invention does not transfer an anionic substituent or fragment thereof to said cation thereby forming a neutral inactive transition metal by product (such as a four coordinate metal structure in the case where the catalyst is a metallocene) and a neutral metal or metalloid by product. Compatible anions are anions which are not degraded to neutrality when the initially formed complex decomposes. The recitation "metalloid", as used herein, includes non-metals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

Improvements in activity, stability, operability and process adaptability can be realized by use of the non-coordinating polyanionic materials herein described. The improvements can be realized because the polyionic activator composition may be prepared in a variety of molecular shapes and sizes, such as small molecular dianions, or as linear, branched, star or crosslinked polyanionic polymers, or as three dimensional polyanionic particles or objects, each of which shape, charge and molecular size is designed to exert a unique influence on the resulting properties of the final polyionic transition metal catalyst. The polyanionic non-coordinating anions, $[(NCA^{b-})_yT]^{by-}$, comprise a central core composition (T) to which a plurality (y) of non-coordinating anionic pendant groups (NCA) of charge b^- are fixed through covalent bonding. As the size of the core 'T' and the charge (the product of 'b' times 'y') increase the size of the polyanionic core material will become large enough to provide a macroscopic heterogeneous catalyst support. In olefin polymerization systems the heterogeneous catalyst comprising the macroscopic polyanionic non-

coordinating anion is capable of controlling product particle size in slurry processes and is amenable to conventional single and series gas phase processes without encountering problems associated with catalyst desorption. Further, the core T may serve to immobilize the cationic transition metal catalyst species with respect to flow of reactant into and product out of a reaction zone wherein a catalyzed reaction, such as polymerization, takes place. In this respect core T may be the reactor walls or other immobile surfaces located within the reaction zone.

Polyionic Catalysts In General

Novel classes of poly-noncoordinating anionic compositions as described hereafter can be used to modify and improve the chemical properties (i.e., activity, selectivity, etc.) and physical state (i.e., homogeneous, heterogeneous) of any catalytic system wherein the catalytically active species is a transition metal coordination cation -- i.e., a transition metal coordinated to fewer ligands than would fully satisfy the coordination number of the transition metal constituent, thus leaving the transition metal in a positive charge and unsaturated state. The role of a non-coordinating anion in such systems is to balance charge without obstructing the coordinatively-unsaturated site on the active transition metal cation. The conversion of an ionic catalyst system of the form $[\text{Catalyst}^{c+}]_{y'}[\text{NCA}^{b-}]$ (where NCA^{b-} is a "non-coordinating anion" of the total charge $b-$ such as BF_4^- , or $\text{B}(\text{Ph}')_4^-$; $c+$ is an integer representing the positive charge on the catalyst and y' the number catalyst cations required to balance charge) into a polyionic catalyst of the form $[\text{Catalyst}^{c+}]_{y'}[(\text{NCA}^{b-})_y\text{T}]^{by-}$ (where the product of $c+$ times $y' = b$ times y) can be accomplished by at

least two general approaches. First, if the monoionic catalyst $[\text{Catalyst}^{\text{C}^+}]_y, [\text{NCA}^{\text{b}-}]$ is prepared from a catalyst precursor and an ion-exchange reagent, $[\text{Ct}^{\text{C}^+}]_{y'}, [\text{NCA}^{\text{b}-}]$ where the product of c^+ times $y' = b$, then the polyionic catalyst may be prepared by an analogous procedure where the catalyst precursor is reacted with $[\text{Ct}^{\text{C}^+}]_{y'}, [(\text{NCA}^{\text{b}-})_y\text{T}]^{\text{by}-}$. Alternatively, the preformed mono ionic catalyst can be combined with $[\text{Ct}^{\text{C}^+}]_{y'}, [(\text{NCA}^{\text{b}-})_y\text{T}]^{\text{by}-}$ under conditions where the desired by-product $[\text{Ct}^{\text{C}^+}]_{y'}, [\text{NCA}^{\text{b}-}]$ and polyionic catalyst $[\text{Catalyst}^{\text{C}^+}]_{y'}, [(\text{NCA}^{\text{b}-})_y\text{T}]^{\text{by}-}$ can be separated by solubility differences. Thus, if the polyanionic activator is insoluble in a solvent where the monoionic catalyst $[\text{Catalyst}^{\text{C}^+}][\text{NCA}^{\text{b}-}]$ is stable and soluble, the ion-exchange process can be done by running a solution of the monoionic catalyst down a column of heterogeneous polyionic activator in much the same fashion as is done in conventional ion-exchange chromatography.

Polyionic Olefin Polymerization Catalyst

The olefin polymerization catalysts of this invention are prepared by combining at least one first component which is a derivative of a transition metal of the Group 3-10 of the Periodic Table of the Elements containing at least one ligand (leaving group) which will react with the cation of a second component. The second component contains, pendant from a core component, a plurality of ion-exchange groups each associated with a cation capable of irreversibly combining with the leaving group ligand liberated by the transition metal first component. Each ion-exchange group comprises a single anionic coordination complex comprising a charge-bearing metal or metalloid element, which anionic complex is chemically bound to the core component and is both bulky and labile,

compatible with and essentially noncoordinating toward the transition metal cation formed from the first component, and capable of stabilizing the transition metal cation without obstructing the transition metal cation's coordinatively-unsaturated site. Additionally, the anion must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization.

All reference to the Periodic Table of the Elements herein shall refer to that format of the Periodic Table of the Elements, published in Chemical and Engineering News, 63(5), 27, 1985 which numbers the groups 1 to 18. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements. Further, in the formulae which follow, unless otherwise indicated, such lettering which appears which is a symbol for an element is intended to indicate that element, i.e., B means boron, Al means aluminum, Ti means titanium. Letters or groupings of letters not otherwise recognizable as symbols for elements are defined in the formulae, i.e., Ct means a "cation," NCA means a "non-coordinating anion," etc., as defined.

The Transition Metal Component

In general any ligand stabilized transition metal catalyst precursor can be activated to its ionic catalytic state by reaction with a polyionic activator composition of this invention. The same general catalytic attributes observed in a monoionic version of the catalyst will likewise be reflected in the polyionic form of catalyst produced by activation of the catalyst precursor with the polyionic activator compositions of this invention. In a monoionic catalyst system various catalyst performance properties

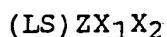
can be influenced by alteration of the ligand structure of the transition metal catalyst precursor, those same ligand affects will likewise be observed in the polyionic catalyst compositions of this invention.

5 However, unlike the monoionic catalyst, in accordance with this invention it is possible to further influence

~~catalyst properties by choice of structure for the~~
anionic moiety of the resulting catalyst. For example

wherein the ligand system of the transition metal
10 catalyst precursor is a chiral ligand system which leads to stereochemical control, this same control will be seen in the polyionic catalyst composition of this invention. Yet by reason of selection of the structure of the polyanionic activator the resulting polyionic
15 catalyst may be improved with respect to its activity, molecular weight capability, selectivity, process adaptability and/or by immobilizing the catalyst for fixed bed operation or other catalyst recover processes.

20 For the olefin polymerization catalyst, the transition metal catalyst precursor is represented by the formula



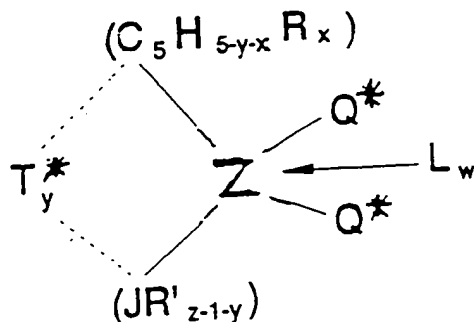
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wherein Z is a group 3 to Group 10 transition metal; X_1 is a leaving group which may be an anionic ligand or a non-coordinating anion; X_2 is hydride or a hydrocarbyl radical; and (LS) is a ligand system comprised of one
30 or more ancillary ligands sufficient to complete the coordination number of Z. Since X_1 is the anionic leaving group, the final catalyst cation will have the structure $[(LS)ZX_2]^+$ after reaction with the polyanionic activator.

35 For an olefin polymerization catalyst the transition metal catalyst precursor compounds may be any transition metal compound which is activatable to a

catalytic state for olefin polymerization by an alumoxane. Such transition metal catalyst precursor compounds thus include (but are not limited to) the Group 4, 5 and 6 metal hydrocarbyloxides as described in WO 92/01006; the Group 4, 5 and 6 metal metallocenes as described in European Patent 0129368 and in US 5 017 714 and US 5 120867, the Group 4 and other metal monocyclopentadienyl-heteroatom ligand compounds as described in US 5 055 438, US 5 096 867, US 5 057 475, US 5 026 798, and EPA 416815; the Group 4 metal amido compounds as described in WO 92/12162; the Group 4 metal metallocenes as described in EPA 277,004, and the like. Those transition metal compounds which are activatable to single sited catalyst systems are the most preferred. These include but are not limited to systems comprising (i) two cyclopentadienyl ligands, each optionally substituted and the two optionally being bridged with a bridging atom or group or (ii) a single, optionally substituted, cyclopentadienyl ligand and a heteroatom - containing ligand, the two ligands optionally being bridged with a bridging atom or group. For example:

1. Monocyclopentadienyl-heteroatom ligand transition metal compounds represented by the formulae:



wherein Z is Zr, Hf or Ti in its highest formal oxidation state (+4, d^0 complex);

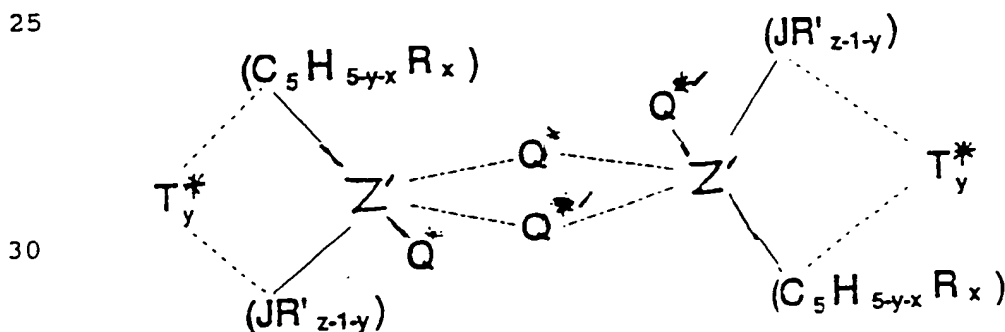
(C₅H₄-xR_x) is a cyclopentadienyl ring which is substituted with from zero to four substituent groups R, "x" is 0, 1, 2, 3, or 4 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C₁-C₂₀ hydrocarbyl radicals, substituted C₁-C₂₀ hydrocarbyl--radicals--wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, and alkoxy radical or any other radical containing a Lewis acidic or basic functionality, C₁-C₂₀ hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group 14 of the Periodic Table of Elements; and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkylborido radicals or any other radical containing Lewis acidic or basic functionality; or (C₅H₄-xR_x) is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C₄-C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl;

(JR'_{z-2}) is a heteroatom ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently a radical selected from a group consisting of C₁-C₂₀ hydrocarbyl radicals, substituted C₁-C₂₀ hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality, and "z" is the coordination number of the element J;

each Q^* is, independently, any hydrolyzable anionic ligand such as a hydride, or substituted or unsubstituted C_1 - C_{20} hydrocarbyl provided that where any Q^* is a hydrocarbyl such Q^* is different from
 5 $(C_5H_4-xR_x)$, or both Q^* together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand;

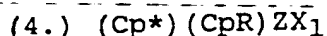
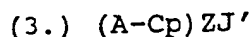
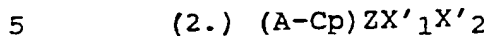
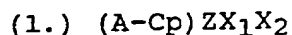
T^* is a covalent bridging group containing a Group
 10 14 or 15 element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;

15 and L is a neutral Lewis base such as diethylether, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n -butylamine, and the like; and " w " is a number from 0 to 3; L can also be a
 20 second transition metal compound of the same type such that the two metal centers Z and Z' are bridged by Q^* and $Q^{*'}$, wherein Z' has the same meaning as Z and $Q^{*'}$ has the same meaning as Q^* . Such compounds are represented by the formula:



With respect to these compounds resort may be had to US
 35 5 055 438, US 5 096 867, US 5 057 475 and US 5 026 798 for further information about specific compounds within this class which would be most preferred for use.

2. Bis(cyclopentadienyl) Group 4 metal compounds represented by the formulae:



wherein "Cp" represents a cyclopentadienyl radical which may be substituted or unsubstituted, and:

10 (A-Cp) is either $(Cp)(Cp^*)$ or $Cp-A'-Cp^*$ and Cp and Cp^* are the same or different cyclopentadienyl ring substituted with from zero to five
15 substituent groups R, and each substituent group R is, independently, a radical which can be hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, or halogen (the size of the
20 radicals need not be limited to maintain catalytic activity, however, generally the radical will be a C_1 to C_{20} radical), or Cp and Cp^* are a cyclopentadienyl ring in which two adjacent R groups are joined forming a C_4 to C_{20} ring to give
25 a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl, or octahydrofluorenyl and A' is a covalent bridging group which restricts rotation of the two
Cp-groups; Z is titanium, zirconium or hafnium; J' is an olefin, diolefin or aryne ligand; X_1 and X_2
30 are, independently, selected from the group consisting of hydride radicals, hydrocarbyl radicals having from 1 to about 20 carbon atoms, substituted-hydrocarbyl radicals having from 1 to about 20 carbon atoms, wherein one or more of the
35 hydrogen atoms are replaced with a halogen atom, organometalloid radicals comprising a Group 14 element wherein each of the hydrocarbyl

substitutions contained in the organic portion of said organometalloid, independently, contain from 1 to about 20 carbon atoms and the like; X'_1 and X'_2 are joined and bound to the metal atom to form a metallacycle, in which the metal atom, X'_1 , and X'_2 form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and R is a substituent, preferably a hydrocarbyl substituent, on one of the cyclopentadienyl radicals which is also bound to the metal atom.

Generally, any metallocene which has heretofore been activated to a catalytic state by reaction with an alumoxane is also suitable for activation by reaction with a polyanionic activator composition of this invention. Illustrative, but not limiting examples of bis(cyclopentadienyl) Group 4 metal compounds which may be used in the preparation of the improved catalyst of this invention are described in EPA 277,003; EPA 277,004, EPA 129368, US 5 017 714, US 5 120 867 and PCT WO 92/00333.

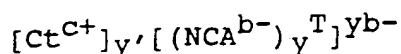
Polyionic Activator Compositions

1. Structural Description of Polyionic Activator Compositions

As already noted, the transition metal compound is activated to a catalytically active state by reacting it with a polyionic activator composition which comprises an atomic, molecular, polymeric, or macroscopic core (T) to which are bonded a plurality of non-coordinating anionic pendant groups (NCA^{b-}). The structure of the polyionic activator compositions comprised of a single type of non-coordinating anions and counter cations can be represented by the following general formula where Ct^{c+} is the counter cation of the

total charge c^+ , y represents the number of pendant NCA-groups; b is the charge on the non-coordinating anion, y' is the number of Ct cations and y times c^+ equals y' times b :

5



Polyionic activator compositions can be comprised of a mixture of non-coordinating anions and/or cations with the only requirement being that the final composition has enough cations to balance the charge. The structural requirements for the pendant non-coordinating anions can vary depending on the reactivity of the catalyst cation used in final catalytically active compositions. Thus, it will be appreciated that catalysts based on late transition metal cations may be compatible with a wider variety of pendant NCA's than those based on early transition metal cations.

20

The anionic portion of a pendant group is chemically bound to the core. By chemically bound, what is meant is a strong bond having greater than 2-3 Kcal and includes covalent, ionic or dative bonds; essentially any bonds other than H-bonds or vander waals forces. Preferably the anionic portion of a pendant group comprises a group represented by the formula:



wherein M is a metal or metalloid selected from the Groups subtended by Groups 3-15; Q_1 - Q_n are, independently, hydride radicals, disubstituted amido radicals, alkoxide radicals, aryloxy radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyls radicals, substituted halocarbyl radicals,

35

hydrocarbyl and halocarbyl-substituted organometalloid radicals; "n" is the number of Q-ligands, preferably no more than one Q being halide, "d" is 0 or 1 and when "d" is 1, D is a bridging group or atom such as hydrocarbyl, halocarbyl, substituted hydrocarbyl, hydrocarbyloxy, aryloxy group, oxo or amido which tethers the non-coordination anion to the core T; and b is the charge on the anion. Compositions wherein each of the Q-ligands of the anionic pendant group are the same or different aromatic or substituted aromatic radical containing from 6 to 20 carbon atoms are preferred. Generally, a mixed anion and/or mixed cation system may be employed in order to fine tune the desired polymer properties. The metal or metalloids may therefore be the same or different.

An anionic group as above described is analogous in many important respects to the single "non-coordinating anion" (NCA) complex described in EPA 277,004 by which the new ionic-transition metal catalyst system as therein described is produced. In EPA 277,004 the catalyst as taught is a discrete complex comprised of one transition metal cation complexed with one non-coordinating anion. As noted, such an anion is essentially non-coordinating to a transition metal cation; that is, although in non-polar low dielectric solvents the anion is weakly coordinated to the catalyst cation to form a "contact ion pair", addition of a Lewis base (L) such as tetrahydrofuran (THF), amines or olefins readily displaces the anion to form charge separated ionic complexes.

In the single anion catalyst systems as described in EPA 277,003 and EPA 277,004 it was found that the performance of the catalyst correlated to the basicity of the non-coordinating anion. Anionic carboranes as described in EPA 277,003 provide a class of catalyst

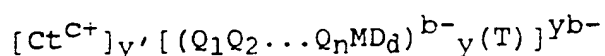
systems of lower activity and lower molecular weight and comonomer incorporation capabilities than that class of catalyst systems described in EPA 277,004 which utilize an anionic coordination complex. Anionic carboranes as a class are stronger bases than are anionic coordination complexes as a class.

It was further found that within that class of catalyst systems which are formed with an anionic coordination complex that anion structure exerted a strong influence on the properties of the catalyst. With respect to the most preferred anionic coordination complex, namely the tetra(pentafluorophenyl)boron anion, hereafter referred to as $[(\text{pfp})_4\text{B}]^-$, replacement of one pentafluorophenyl ligand (pfp) with a hydrocarbyl ligand such as methyl, butyl, phenyl or a polystyrene group produced a catalyst with lower molecular weight and comonomer incorporation capabilities.

Relative to the most preferred class of monoionically activated transition metal catalyst systems, i.e. those wherein $[\text{Q}_1\text{Q}_2\ldots\text{Q}_n\text{M}]^-$ is the non-coordinating anion, to further improve the product and process versatility and operability of an ionic catalyst system it has been found to be necessary to have available a wide variety of possible anion structures where the charge, shape, size, and negative charge distribution of the non-coordinating anionic activator composition can be varied.

In this invention, the chemical properties of the activating anion composition are varied by producing it in the form of a polyionic activator composition the molecular core of which can be controlled in terms of its size and shape, as well as providing for control of the extent and position of the negative charge

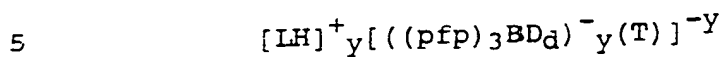
localization within the composition. The polyionic activator compositions can be produced in a range of sizes from that of a simple molecular size for production of soluble catalyst systems to that of macroscopic polyionic activator compositions which are large enough to function as a heterogeneous support for use of the catalyst in fluidized bed, slurry or fixed bed polymerization processes. The polyionic activator compositions comprising a single type of counter cation and pendant non-coordinating anion which are suitable activators are of the formula:



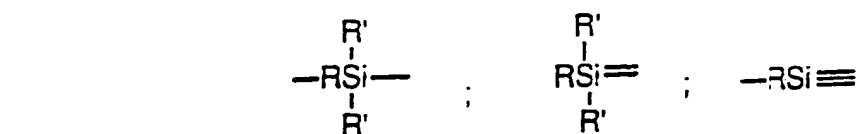
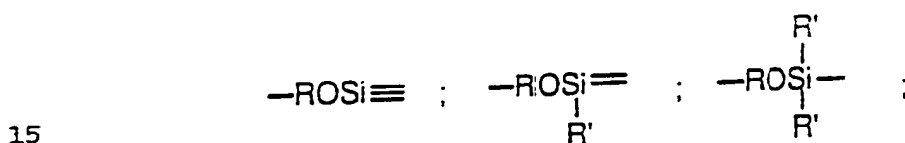
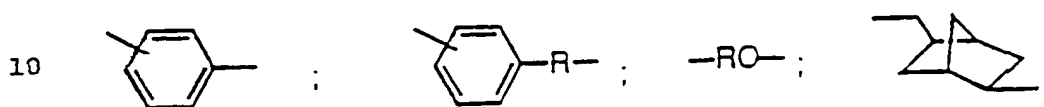
wherein:

- 15 Ct is a cation capable of reacting with an early transition metal alkyl complex, such as trialkylammonium, Ag^+ , Ph_3C^+ , oxonium, or tropylium;
- M is, a metal or metalloid from Group 3-15;
- 20 Q_1-Q_n are, independently, hydride radicals, disubstituted amido radicals, alkoxide radicals, aryloxy radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, hydrocarbyl and halocarbyl-substituted organometalloid radicals;
- "n" is the number of Q ligands bonded to M;
- "d" is 0 or 1 and when "d" is 1, D is a diradical hydrocarbyl, halocarbyl, substituted hydrocarbyl, hydrocarbyloxy or aryloxy, oxo, imido, or sulfido group which tethers the anion to the core T;
- 30 T is an atomic, molecular, polymeric or macroscopic polyradical moiety capable of coordination with M or with D; "y" is an integer greater than one and represents the number of pendant non-coordinating anions, b is the charge on the anionic pendant groups, c+ is the charge on
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The polyanion composition most preferred for use in preparing catalysts of this invention are of the formula:



wherein B is boron and D is a group of the formula:

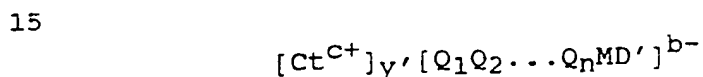


In general the polyionic activator can be prepared by at least two general synthetic approaches. In one general method, the polyionic activator compound is prepared from a "synthon" compound of the formula $[Ct^{c+}]_{y'}[(Q_1Q_2\dots Q_nMD')^{b-}]$ wherein M, Ct, c+, b-, and Q_n are as previously defined, and D' is a radical group which contains at least one functional group which is polymerizable or otherwise reactive with a substrate (T') to bond therewith, y' is the number of c+ cations and y' times c+ equals b-. The polyionic activator compound is prepared by reacting a synthon compound with a coupling agent polymerization initiator and optionally comonomer, or other substrate (T') under conditions suitable to cause reaction of the D' functional group of the synthon compound to yield $[Ct^{c+}]_{y'}[(Q_1Q_2\dots Q_nMD_d)^{b-}_y(T)]^{yb-}$. If necessary, the

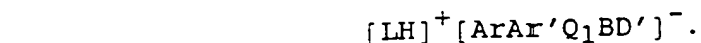
initial cation, Ct^{C+} , can be exchanged for other more reactive cations using standard chemical techniques. In a second general method (where $D_d = D_0$), the polyionic composition can be prepared by reacting the neutral Lewis acid $Q_1Q_2...Q_nM$ with a polyionic preformed core $[Ct^{C+}]_{y'}[T'']^{Y-}$ to form $[Ct^{C+}]_{y'}[(Q_1Q_2...Q_nM)_yT'']^{Y-}$ where T'' is a polyanionic Lewis basic core substrate and y' times $c+$ equals $y-$.

10 A. Synthons

Compounds which are useful for the synthesis of the polyanion compositions as described above are of the general formula:



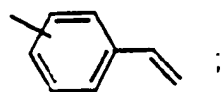
and referred to herein as "synthons" wherein D' is a radical group which contains at least one functional group which is polymerizable or otherwise reactive. A preferred class of the synthon compounds are those of the formula:



The compounds most preferred as synthons are of the formula:



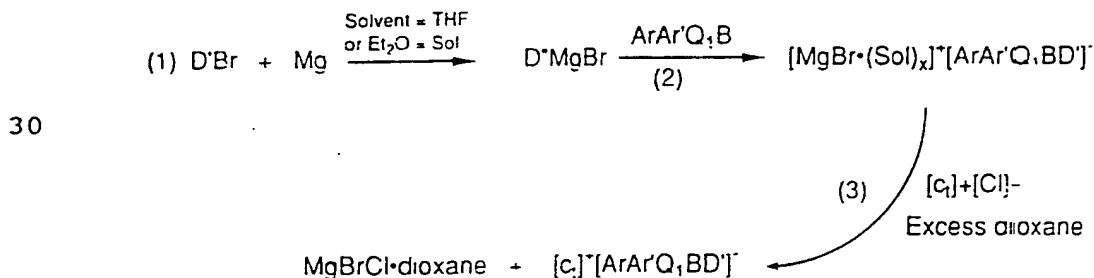
wherein D' is a group of formula:



wherein R is hydrocarbyl such as phenyl, n-propyl,
5 methylenenorbornenyl, or cyclohexyl; each R_j is
independently hydrocarbyl or substituted hydrocarbyl, X
~~is a halide or alkoxide and j is an integer between 0~~
and 2.

10 B. Preparation of Synthons

Synthons may readily be prepared by reacting a Grignard reagent (BrMgD') with a neutral boron compound ($\text{ArAr}'\text{Q}_1\text{B}$) to form the solvated MgBr^+ -salt of the desired functionalized synthon $[\text{ArAr}'\text{Q}_1\text{BD}']^-$. The MgBr^+ -salt can be easily converted into a variety of desirable Ct^+ -salts in water, THF, ether, or methylene chloride by treatment with $[\text{Ct}]^+[\text{Cl}]^-$ and dioxane (unless water is the diluent, in which case dioxane is not necessary because the desired product is insoluble in water under conditions where the magnesium dihalide dissolves completely). Dioxane is used to facilitate the precipitation of the magnesium halide salt as shown below.



35

In an alternative method, the Mg and the boron reagents are first combined in an ether solvent (tetrahydrofuran, THF) and the bromide reagent (D'Br) is then added. In this method the Grignard reagent is generated in situ and then is quickly converted by the boron reagent to the stable synthon product.

Production of the synthon compound in high yield through a Grignard reagent intermediate as above described may be accomplished under those conditions of temperature and with those solvents which are conventionally used in preparing a Grignard reagent. As is known to those skilled in the art of Grignard reactions, if the bromide reagent contains other functional groups which are adverse to the formation of a Grignard reagent, such as for example a hydroxide group, it must first be converted to a Grignard non-reactive group such as a trimethylsiloxane or a tetrahydropyranyl ether (THP) group, i.e., if D' has any sensitive groups, they must first be "protected". One of ordinary skill in the art can employ standard organic protecting group concepts in this invention. For example, 4-bromostyrene and bromonorbonylene may be used without further modification in the preparation of the Grignard intermediate reagent whereas 3-bromopropanol cannot. It would be necessary to use a protected bromopropanol to form an stable Grignard reagent.

The initially formed MgBr^+ -salt can be converted into a more well-behaved Ct^+ -salt such as a Li^+ , Et_4N^+ , or trialkylammonium-salt, using standard metathetical procedures including ion-exchange chromatography. Thus, the initially formed $\text{MgBr} \cdot (\text{THF})_x^+$ salt of the synthon may be converted into the Li^+ , Na^+ , or Ct^+ -salt by running a solution of magnesium bromide-precursor down a cation-exchange column containing a

commercially available ion-exchange resin, such as Amberlyst XN-1010 or Amberlite IRP-69 resin, [a registered trademark of Rohm and Haas Co., located at Independence Mall West, Philadelphia, Pennsylvania, 19105 Phone: (215) 592-3000] which has been pretreated or loaded with the desired cation. The procedures for pretreating and using ion-exchange resins are well-established and may be employed in this invention. These salts are preferred over the MgBr^+ -salt because they can be isolated as crystalline products and because they can be more easily converted into the final polyanionic form. The preparation of several salts of $(\text{pfp})_3\text{B}(4\text{-styrene})^-$ and $(\text{pfp})_3\text{B}(\text{methylenenorbornylene})^-$ are given in the Examples Section. The preparation of an alcohol functionalized synthon can be accomplished in a similar fashion using a THP-protected alkylhalide. The Grignard reagent is formed in THF, and the anion is prepared from the stable protected Grignard reagent by treatment with $\text{B}(\text{pfp})_3$. Conversion of the MgBr^+ -salt into the trialkylammonium salt can be done in water using excess ammonium halide. In many cases these conditions are sufficient to catalyze the deprotection of the alcohol and the final alcohol functionalized synthon $[\text{R}'_3\text{NH}][(\text{pfp})_3\text{B-R-OH}]$, can be formed in one step.

Silylhalide functionalized synthons can be prepared from the norbornylene- and styrene-functionalized synthons using standard hydrosilation procedures as indicated in Figure 1 routes 4 and 5. Likewise, the alcohol functionalized synthons can be converted into silylhalide analogs by treatment with $\text{R}'_j\text{SiCl}_{4-j}$ ($j = 0$ to 3) and tertiary amine (to adsorb the liberated HCl) as in Figure 1 route 6 to synthon 6.

2. Preparation of Polyanion Compositions From the Coupling or Polymerization of Synthons

5 Synthons compounds may be converted to a polyanion composition by well established synthetic techniques such as anionic, cationic, free radical, ring opening (ROMP), conventional Ziegler-Natta and metallocene based olefin polymerization catalysis, as well as by an
10 assortment of hydrolysis and other 'condensation' reactions. Figure 1 depicts in summary fashion some of the variety of techniques by which a synthon compound may be converted to a polyionic activator composition.

As illustrated by Figure 1 a synthon may be
15 polymerized or copolymerized to yield a variety of specifically shaped polyanion compositions. It should be appreciated by those of ordinary skill in the art that there are literally an infinite number of chemical methods available for coupling, or polymerizing
20 substituted norbornylenes, styrenes or alcohols to form a discrete or polymeric material. Most of this art was applied to simple, non-ionomeric monomers. This invention couples or polymerizes monomers which are bulky and have a net negative charge. If charge or
25 steric bulk prematurely stop polymer growth, a few equivalents of a neutral spacer comonomer can be added to allow further activator polymerization. It should be noted that in some cases living anionic and living ROMP [ring opening metathesis] polymerization
30 techniques can be employed to create block, star, and end functionalized polyionic activators.

Polyanions meeting the design criteria can be prepared by a variety of chemical approaches. This concept described herein provides a continuum of
35 catalyst systems ranging from homogeneous to heterogeneous as the size and charge of the polyanion increases. At some point in each of the described

approaches the polyanionic activator can be prepared as a macroscopic particle which itself can function as a heterogeneous support in slurry, bulk gas phase, processes and fixed bed. When linear polymers are prepared the individual polyanionic units can entangle or aggregate together to form macroscopic particles that function as both activator and catalyst-support

The following are illustrative, but not limiting, examples of techniques for preparing polyanion compositions having specific features of size, shape and charge distribution.

A. Polyionic Activators From Norbornylene Functionalized Synthons

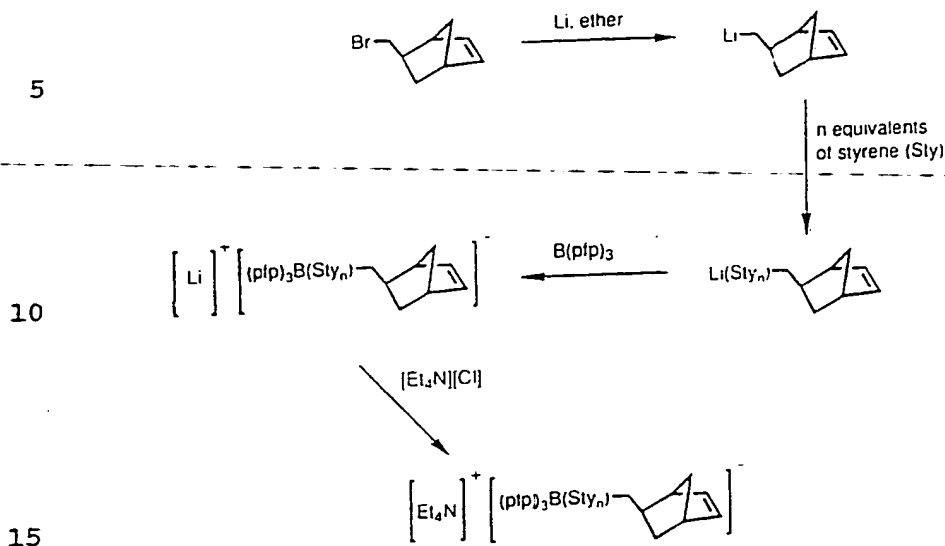
As indicated in Figure 1 routes E and F, norbornylene terminated synthons can be converted into linear or crosslinked polymeric polyanions using catalysts and initiators which are known to affect the polymerization or copolymerization of common norbornylene derivatives. Substituted norbornylenes can be polymerized by cationic, Ziegler-Natta, ring opening metathesis and Group 4 metallocene olefin polymerization catalysts. In each case, the structure of the polyionic activator composition (linear or crosslinked) and the concentration of pendant ionic centers can be controlled by use of various amounts of comonomers (such as norbornylene) and/or crosslinking agents (such as norbornadiene) during the polymerization reaction. Figure 1 routes E and F begins with a synthon in which the methylene norbornylene functionality is directly bonded to the boron anion through the methylene [where "SP" is the spacer unit and is illustrated equal to zero], or through a suitable spacing moiety, 'SP'. The spacing unit 'SP' serves to bridge the functional groups of the system to the boron center and is a hydrocarbyl or

halocarbyl diradical containing from about 1 to 10,000 carbon atoms such as methylene or polystyrene. As discussed above, the norbornylene functionalized synthon can be isolated with a variety of counter cations. It will be appreciated by those of ordinary skill in the art that the cation in the the synthon needs to be chosen so as to avoid potential incompatibilities with the particular polymerization system being used in the preparation of the polyionic activator. Thus, when preparing a polyionic activator using an olefin polymerization catalyst one must avoid the presence of labile Lewis Bases which may be associated with the counter cation (for example $\text{MgBr} \cdot (\text{THF})_x$). The choice of counter cation may also play a role in the thermal stability of the synthon salt.

The homopolymer of the synthon $[\text{DMAH}][\text{B}(\text{pfp})_3\text{nb}]$ (where $\text{DMAH} = \text{PhMe}_2\text{NH}^+$, and nb=methylene-norbornylene) was prepared by the addition of a catalytic amount of Cp_2HfMe_2 (where Cp is cyclopentadienyl and Me is methyl). The hafnocene precursor reacts with a portion of the synthon to produce an active olefin polymerization catalyst $[\text{Cp}_2\text{HfMe}(\text{NMe}_2\text{Ph})][\text{B}(\text{pfp})_3\text{nb}]$ which slowly catalyzes the polymerization of the anions through the unsaturated norbornylene substituent to produce a glassy low molecular weight linear polyionic activator.

In many cases when the spacing unit 'SP' is small or non-existent the functional groups, such as norbornylene, may be so close to the charge bearing center (i.e. the boron atom) that the chemistry of the functional group is affected. As the size of 'SP' increases the chemistry of the functional groups becomes standard and the desired polyanion can be synthesized using established procedures. The norbornylene synthon, $[\text{Et}_4\text{N}]^+[\text{B}(\text{pfp})_3(\text{STy})_n\text{-nb}]^-$ where $(\text{STy})_n$ represents polystyrene can be prepared in a

three step procedure starting from lithium methylene norbornylene as shown below



[Et₄N][B(pfp)₃(SP-nb)] (where 'SP' is a linear polymer such as polystyrene) can be copolymerized with ethylene in toluene at low pressure by the addition of a small amount of a ionic hafnium catalyst (Cp₂HfMe(NMe₂Ph)][B(pfp)₄]. The granular ethylene copolymer can be washed with methylene chloride containing excess [DMAH][Cl] to exchange DMAH⁺ for Et₄N⁺ and form the final polyionic activator. Similar procedures can be employed to prepare polyionic activators derived from other polyolefin backbones by proper choice of catalyst (chiral metallocene and propylene for isotactic backbones, or fluorenyl-based metallocenes for syndiotactic backbones) and monomers. As indicated in Figure 1 route 5, the norbornylene synthon may also be converted into polyionic activators using hydrosilation chemistry (i.e., platinum oxide catalysts and HSiR_jX_{3-j}) to introduce a silicon halide or alkoxide functionality (i.e. X) on the norbornylene substituent followed by various hydrolysis procedures (see Figure 2 and 3).

B. Polyanions From Styrene Functionalized Synthons

As illustrated in Figure 1, route D, a styrenic
5 synthon may be polymerized by a variety of techniques
to yield a polyanion composition of various properties.
Again, 'SP' is defined as a spacing unit containing
from about 1 to 10,000 carbon atoms bridging the boron
anion to the functional groups. These include the
10 homo- or copolymerizations via free-radical, cationic,
anionic or thermal mechanisms. The use of emulsion
polymerization technology in combination with the free
radical polymerization process can be designed to yield
microporous polyanionic polymeric gels or bead
15 compositions. The synthesis of a synthon reagent
having styrenic functionality is straightforward from
4- bromostyrene, magnesium, and B(pfp)₃. A variety of
polyanionic crosslinked polymers are accessible by the
free radical, cationic, or anionic polymerization of a
20 styrenic synthon reagent in the presence of
divinylbenzene. Again, there are many opportunities for
synthetic control over the size, topology, charge and
porosity of the final product.

The staged addition of styrenic synthon monomer at
25 the end of the polymerization of the crosslinking
reagent will allow for the formation of a "skin" or
surface concentrated content of fluorinated activator
coating the exterior of the styrenic micropores.

Another important use of this synthon is to
30 convert the pendant styrenic olefin into a silicon
halide or alkoxide using a silane, HSiR'_jX_{3-j}, where X
is alkoxide or halide and a standard hydrosilation
catalyst as shown in Figure 1, route to complex 4. The
use of silyl halide or alkoxide coupling reagents to
35 prepare polyanionic activators is discussed in the next
section.

**C. Polyionic Activators From
Hydroxy-Functionalized Synthons.**

As indicated in Figure 1, route A, hydroxy functionalized synthons can be used to prepare discrete polyanions by reaction with metallic halides in the presence of an HCl-trap such as trialkyl amines. Thus, the trianion, $[\text{PhSi}(\text{OPh}-(\text{SP})\text{B}(\text{pfp})_3)_3]^{3-}$, can be prepared by reacting PhSiCl_3 with three equivalents of $[\text{Ct}]^+[\text{B}(\text{pfp})_3(\text{SP}-\text{PhOH})]^-$ in the presence of poly-4-vinylpyridene. Other approaches for preparing polyionic activator compositions from hydroxy functionalized synthons include: acid catalyzed dehydration of hydroxylated surfaces (such as amorphous silica and mineral silicates), and esterification or transesterification of discrete or polymeric materials containing more than one carboxylic acid or ester per molecule, polymer chain or particle.

**D. Polyanions From Silylhalide
Functionalized Synthons**

As illustrated by Figure 1, routes C and B and Figures 2 and 3 polyanionic compositions can be prepared from synthons with silyl halide or alkoxide functionalities. This part of the invention utilizes well established fields of organometallic and solid state synthesis to prepare novel polyionic activator compositions from the special ionomeric monomers or synthons described above.

The synthesis of silicates by the controlled hydrolysis of $\text{R}'_j\text{SiX}_{4-j}$ is a well developed field of technology when R' is a normal organic substituent such as methyl or phenyl. The physical properties of the resulting crosslinked polymer can be controlled by adjusting the ratios of the monomer components (i.e. the amount of SiX_4 , $\text{R}'\text{SiX}_3$, and $\text{R}'_2\text{SiX}_2$ etc.). A

continuum of polymeric materials can be prepared which range from brittle inorganic solids (monomers where $j = 0$ or 1) to rubbery organometallic polymers (where a significant amount of $j = 2$ and 3 chlorosilane monomers are added). Other important structural variables such as molecular weight and sequence distribution of comonomers can be controlled by adjusting the pH, the concentration, temperature and time of reaction (for M_w control), and staging or sequencing the addition of comonomer (for sequence distribution control). Most of the work on the classical systems of polysilicate synthesis was carried out using water as the solvent and the final products are poorly defined silicate materials known as "sol-gels". More recently polysilicates have been prepared by the controlled hydrolysis of silylhalides in organic solvents such as toluene, or methylene chloride. The results of this more recent procedure indicates that silicate synthesis in organic solvents using stoichiometric amounts of H_2O (needed to convert the silylhalide to the silanol) can be a more selective and reproducible method of preparing low molecular weight materials than analogous reactions carried out in basic water. This technology can be used to form polyanionic compositions by preparing and hydrolyzing anionic coupling reagents $(NCA)_jSiX_{4-j}$ where NCA preferably is $[(pfp)_3B-D]^-$. The distance from the boron atom to the silicon atom in the coupling reagent can be varied over a large range by replacing "bridging group" ($-SP-$) with linkages of different size such as phenyl, propyl, biphenyl, and styrene oligomers. A simple example of this concept is for the controlled hydrolysis of $[(pfp)_3B-SP-PhSi(OMe)_3]^-$ as shown in Figure 2. The reaction in Figure 2 and Figure 3 are included for the purposes of clarifying the concept and are not intended to indicate that single, well defined polyanions, would be produced under hydrolysis conditions.

The reaction can also be carried out in the presence of neutral, smaller comonomers such as $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ to control or modify degree of polymerization and total charge. The polymerization process may yield polyanion compositions having exposed and reactive Si-OH groups. The exposed silanol groups can be protected with smaller organosilicon head groups such as $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiMe}_2\text{X}$. Another level of control is to do sequential additions of a neutral silicon halide crosslinking agent and a synthon reagent. A simple and potentially useful example would be to create a central crosslinked core (T) by the controlled hydrolysis of SiX_4 followed by the delayed addition of synthon agent to "cap" the outermost silicon hydroxyls on the central core with non-coordinating anions to form small particles of silica (T) with anions on the "skin" as shown in Figure 3, where R represents the bridging spacer unit and the functional lead group. The silicates depicted in Figure 3 are intended to represent a slice of three-dimensional solid which may be prepared under hydrolysis conditions. The hydroxy- and activator functional groups on the silicon atoms which are not located in the plane of the paper have been excluded for the purposes of clarity.

As illustrated by Figure 1, view C, a synthon may be coupled to a wide variety of hydroxylated substrates such as silica gel, alumina, metal oxides, polymers, or membranes which have polyhydroxylated surfaces. Figure 1B shows how silyl halide or alkoxide anionic coupling reagents 4, 5 or 6 can be polymerized using standard hydrolysis procedures to give linear, branched or crosslinked polyanionic siloxanes or siliates.

3. Preparation of Polyionic Activators From Preformed Polyionic Core Substrates

The second general method of preparing polyionic activators involves the reaction of a preformed polyionic core $[Ct^{C+}]_y[T^{Y-}]$ with an excess of a suitable Lewis Acid, as shown in Figure 4, where C^{C+} is lithium cation and the neutral Lewis Acid is $B(pfp)_3$. This approach can be used to prepare a wide variety of discrete and heterogeneous polyionic activator compositions. The synthetic approach will yield useful polyionic activators from any preformed polyionic core precursor if two design criteria are met: 1) the anionic pendant group $-R^-$ (as shown in Figure 4) must be sufficiently basic to form a stable coordination complex with $B(pfp)_3$ and 2) the substrate T'' must not contain accessible chemical functionalities which act as catalyst poisons. The chemical compatibility of a particular core T'' with the metallocene catalyst cation, and the reactivity of a selected pendant group $-R^-$ with the Lewis Acid ($B(pfp)_3$) are easily predicted using known reactivity patterns. If it is chemically reasonable that the model compound $[Ct]^+[H-R]^-$ would react with $B(pfp)_3$ to form a stable salt $[Ct]^+[B(pfp)_3(R-H)]^-$, and if the resulting boron anion would be expected to function as a stable non-coordinating anion in the metallocene catalyst system (i.e. if $B(pfp)_3(R-H)^-$ is stable to hydrolysis by water) then the scheme shown above will yield a suitable polyionic activator (unless the core T'' is itself a catalyst poison). Core substrates which expose high concentrations of chemical functionalities which are known poisons for metallocene polymerization catalysts (polar functionalities such as carboxylates, acid protons, organic halides, esters, ketones, aldehydes etc.) should be avoided. In some cases, such as when silica is the substrate and hydroxyl-groups are present on the surface, the reactive functionality can be masked or protected using standard chemical treatments.

Illustrative but not limiting examples of polyionic activators prepared from preformed core substrates are described below.

5 A. From Crosslinked Polystyrene Core Substrates

Polystyrene supported polyionic activators can be prepared by two distinct methods. The first approach
10 involves modification of preformed crosslinked polystyrene beads which can be purchased or prepared using emulsion polymerization procedures. The general approach is shown below for a crosslinked styrene/chloromethylstyrene copolymer. Lithiated
15 polystyrene beads can be prepared by a variety of established procedures. When the chloromethylstyrene copolymer is used lithiation yields pendant groups having a benzyl anion structure and it is known that benzyl anions (e.g. BzLi) form stable anionic
20 coordination complexes with B(pfp)₃. Thus, a variety of microporous polystyrene polyionic activators can be prepared using the scheme shown in Figure 5.

A second general approach for preparing polyionic activators containing crosslinked polystyrene
25 substrates is to use anionic polymerization techniques to prepare a crosslinked polystyrene (or other anionically prepared polymer backbone) core with pendant living lithium polystyrene groups as shown in Figure 6. This approach is quite general and will work
30 for any polymer backbone which can be synthesized using living anionic polymerization techniques. The size, concentration of pendant ionic groups, and the physical properties of the core "T" can be varied by adjusting the amount of crosslinking agent, the monomer to
35 initiator ratio, the solvent, the concentration of monomer, the selection of monomer(s), and the time of reaction in the core forming step.

B. From Polydivinylbenzene Core Substrate

The scheme Figure 7 shows how linear and crosslinked lithiated polymers can be prepared using divinylbenzene and an anionic initiator. The molecular weight of the final product can be varied by adjusting the reaction time, temperature, and solvent. Long reaction times, higher temperatures and better solvents yield higher molecular weight products. Reaction of the lithiated polymer with excess Lewis Acid (preferability $B(pfp)_3$), followed by the standard $[DMAH][Cl]$ treatment yields polyionic activators, as illustrated in Figure 7 where DVB represents divinylbenzene.

C. From Surface Modified Glass, Silicas, and Metals

The use of silane coupling reagents of the form R_xSiX_{4-x} (where each R is an organic radical and X is either halide or alkoxide) to modify the hydroxylated surface of glass or silica is a well established field. This technology can be used to coat the surface of hydroxylated surfaces with a wide variety of R-functionalities. The scheme illustrated in Figure 8 exemplifies a bromobenzene functionality covalently bonded to a silica surface using a mixture of $BrPhSi(OMe)_3$ and $PhSi(OMe)_3$. The concentration of bromobenzene functionality can be varied by adjusting the ratio of the two silicon coupling reagents. Treatment of the surface modified silica with excess $t-BuLi$ in ether or THF at $-78^\circ C$ converts the bromobenzene functionality into a basic aryllithium reagent. The reaction is filtered, washed with THF or ether, suspended in ether, and treated with excess $B(pfp)_3$. The solid is isolated by filtration, washed

with excess toluene, dried and placed in a narrow chromatographic column. The silica is slowly eluted with a THF solution of [DMAH][Cl] (large excess) to affect the exchange of DMAH-cation for the lithium counter-ion. The column is then eluted with a large excess of pure methylene chloride to remove excess [DMAH][Cl] and coordinated THF. The product is dried in vacuum at elevated temperature for 24 hours yielding a polyionic activator where the core T has a high surface area of silica. Similar procedures may be used to prepare polyionic activators from other hydroxylated surfaces such as glass, alumina, or polymers containing hydroxide-functionality such as aluminum, zirconium, tin, titanium, and nickel.

4. Preparation of the Catalyst System

The improved catalyst compositions of the present invention will, preferably, be prepared in a suitable solvent or diluent. Suitable solvents or diluents include any of the solvents known in the prior art to be useful as solvents in the polymerization of olefins, diolefins and acetylenically unsaturated monomers. Suitable solvents include but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane and the like; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene and the like. Suitable solvents further include basic solvents which are not generally useful as polymerization solvents

when conventional Ziegler-Natta type polymerization catalysts are used such as chlorobenzene.

In general, and while most transition metal compounds identified above may be combined with most
5 activator compounds identified above to produce an active olefin polymerization catalyst, it is important to continued polymerization operations that either the metal cation initially formed from the transition metal compound, or a decomposition product thereof, be a
10 relatively stable catalyst. It is also important that the anion of the activator compound be stable to hydrolysis when an ammonium salt is used. Further, it is important that the acidity of the activator compound be sufficient, relative to the transition metal
15 compound, to facilitate the needed reaction of the cation portion of the activator with a ligand of the transition metal compound. Conversely, the basicity of the transition metal compound must also be sufficient to facilitate the needed reaction. In general,
20 transition metal compounds which can be hydrolyzed by aqueous solutions can be considered suitable compounds for forming the catalysts described herein.

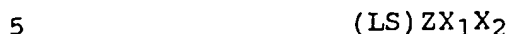
As before discussed, the active catalyst species of the catalyst of this invention is relatively stable
25 and is not subject to the ion equilibrium deactivation as are alumoxane cocatalyzed transition metal catalyst systems. Unlike metallocene-alumoxane catalyst systems wherein, to obtain a practical level of catalyst productivity it is generally required to use an amount
30 of alumoxane, measured as aluminum atom, to provide a ratio of Al:transition metal well in excess of 1000:1, catalysts of this invention which are highly productive may be prepared at ratios of metallocene to activator in an amount which provides a ratio of metallocene
35 molecules to a number of pendant anion groups of the activator composition of 10:1 to about 1:1, preferably about 3:1 to 1:1. The degree of "polyanionicness" of

an activator composition - i.e., the number of pendant anionic groups contained by a given quantity of activator compositions - may be readily determined by titrating an aqueous solution of it to a neutral pH with a base such as NaOH.

In general the catalyst system of this invention can be prepared by combining a transition metal compound or metallocene having at least one substituent ligand which is hydrolyzable with water with a polyanion activator composition as described above in a suitable hydrocarbon solvent at a temperature within the range of from about -100° C to about 300° C, preferably from about 0° C to about 100° C, and allowing the two components to react.

In general, the stable catalyst formed by the method of this invention may be separated from the solvent and stored for subsequent use. The less stable catalyst, however, will, generally, be retained in solution until ultimately used in the polymerization of olefins, diolefins and/or acetylenically unsaturated monomers. Alternatively, any of the catalysts prepared by the method of this invention may be retained in solution for subsequent use or used directly after preparation as a polymerization catalyst. It will, of course, be appreciated that the catalyst system will form in situ if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization step. While the catalysts do not contain pyrophoric species, the catalysts' components are sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere such as nitrogen, argon or helium.

In preferred embodiments of the invention the transition metal compounds used to form the catalyst composition are of the formula



wherein:

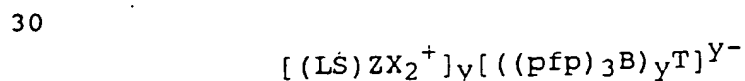
Z is a group 3 to 10 transition metal, X_1 is an anionic leaving group ligand or a non-coordinating anion leaving group, X_2 is a hydride or hydrocarbyl ligand, and (LS) is a ligand system which completes the coordination number of Z.

Preferably, the transition metal compound has a ligand system (LS) coordinated to the transition metal which comprises (i) two cyclopentadienyl ligands, each optionally substituted and the two optionally being bridged with a bridging atom or group or (ii) a single, optionally substituted, cyclopentadienyl ligand and a heteroatom - containing ligand, the two ligands optionally being bridged with a bridging atom or group.

In particular it is preferred to use such transition metal compounds where each of X_1 and X_2 is independently an alkyl group such as methyl.

The preferred polyanionic activator composition has $(pfp)_3B$ non-coordinating anionic groups bonded to the core.

Reaction of the transition metal compound with the preferred activator composition therefore yields an active catalyst composition represented by the formula



In the case where the balancing cation of the activator composition is a Bronsted acid LH^+ , the Lewis base L liberated during catalyst formation either remains in solution or is weakly associated with the transition metal cation center. Ammonium cations are

the preferred balancing cation component of the activator composition.

In summary, a polyanionic activator moiety may be prepared from an intermediate compound in which the metal or metalloid element of the NCA group is chemically bonded to a reactive functional group, said radical being chemically-reactable with the core component, or being polymerizable with other intermediates compounds and optionally other comonomers to form the core component.

5. Polymerization Process

In general the improved catalyst of this invention will polymerize olefins, diolefins and/or acetylenically unsaturated monomers either alone or in combination with other olefins and/or other unsaturated monomers at conditions well known in the prior art for conventional Ziegler-Natta catalysis. The catalyst may be used to polymerize ethylene, α -olefins and/or acetylenically unsaturated monomers having from about 2 to about 18 carbon atoms and/or diolefins having from about 4 to about 18 carbon atoms either alone or in combination. The catalyst may also be used to polymerize ethylene, α -olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers.

In the polymerization process of this invention, the molecular weight appears to be a function of both polymerization temperature and pressure. The polymers produced with the catalyst of this invention, when prepared in the absence of significant mass transport effects, will, generally, have relatively narrow molecular weight distributions.

In general, catalysts can be selected so as to produce the polymer products which will be free of certain trace metals generally found in polymers

produced with Ziegler-Natta type catalysts such as aluminum, magnesium, chloride and the like. The polymer products produced with the catalysts of this invention should, then, have a broader range of applications than polymers produced with more conventional Ziegler-Natta type catalysts comprising a metal alkyl, such as an aluminum alkyl.

In a preferred embodiment, the catalyst, immediately after formation, will then be used to homo- or copolymerize lower olefins particularly ethylene or propylene, at a temperature within the range from about 0° C to about 100° C and at a pressure within the range from about 15 to about 500 psig. In a most preferred embodiment of the present invention, the most preferred catalyst for the formation of ethylene based polymers will be used either to homopolymerize ethylene or to copolymerize ethylene with a lower α -olefin having from 3 to 6 carbon atoms, thereby yielding a plastic or an elastomeric copolymer. In both the preferred and most preferred embodiments, the monomers will be maintained at polymerization conditions for a nominal holding time within the range from about 1 to about 60 minutes and the catalyst will be used at a metallocene concentration within the range from about 10^{-5} to about 10^{-1} moles per liter of diluent.

Polymerization may also occur with the inventive catalyst wherein the activated catalyst composition is immobilized with regard to a fluidized flow of monomer or polymer, which process comprises maintaining monomer in fluidized contact with the immobilized activated catalyst composition at a temperature and for a time sufficient to polymerize at least a portion of the olefin to a polyolefin, and removing the polyolefin from contact with the activated catalyst composition.

EXAMPLES

Example 1

In 100 mls of diethylether (Et₂O) containing 2.0 g
5 of Mg metal shavings (pretreated with 1,2 dibromoethane
to clean surface) 10.5 g of 2-bromomethy-5-norbornene
was added dropwise at room temperature under rapid
stirring. The formation of the Grignard reagent
proceeded quickly to form a light amber solution. The
10 solution was filtered to remove the excess Mg metal to
yield 93 mls of Grignard reagent. Thereafter, 4.6 g of
tripentafluoro-phenyl boron was added to 15cc of the
Grignard reagent in 50 ml of Et₂O. The mixture was
stirred for 10 minutes at room temperature before
15 pentane (50 ml) was added to precipitate a white ionic
solid. The solid was collected by filtration, washed
with pure pentane and dried in vacuum. The ¹H NMR
spectrum of the solid in d₈-THF was dominated by THF
signals but a clean multiplet was observed at 6 ppm
20 which are characteristic for the inequivalent olefinic
protons on the norbornylene group (nb) of a composition
of the structure [MgBr THF_x]⁺[(pfp)₃Bnb]⁻. High field
¹³C NMR spectroscopy verified the structure.

25 Example 2

5.28 g of the glassy white solid precipitate
prepared in Example 1 was suspended in 100 mls of water
at room temperature after which 1.15 g of
dimethylanilinium hydrochloride was added to the
30 solution and stirred for 10 minutes. The reaction
mixture was transferred to a separatory funnel and was
extracted with methylene chloride (2 times with 50
mls). The methylene chloride layers were combined and
washed 3 times with 50 mls of water to remove excess
35 dimethylanilinium hydrochloride. Thereafter the
methylene chloride extracts were dried using Na₂SO₄,
filtered. The product was crystallized from methylene

chloride concentrates at low temperature to yield 2.9 grams of $[\text{DMAH}]^+[(\text{pfp})_3\text{Bnb}]^-$.

Example 3

5 1.g grams of $[\text{DMAH}]^+[(\text{pfp})_3\text{Bnb}]^-$ prepared as in Example 2 was suspended in 25 mls of toluene to give a two phase liquid (top phase toluene rich, bottom phase boron reagent rich). 0.06 g of Cp_2HfMe_2 was added to the well stirred mixture at ambient temperature causing
10 an immediate temperature increase of 1-2 degrees ($23-25^\circ\text{C}$). After 30 minutes a yellow oil precipitated from solution. The oil was isolated, washed with pure toluene (three time with 20 mls), and dried to yield 0.8 grams of a glassy solid. The solid was dissolved
15 in methylene chloride and washed three time with water to remove catalyst residue. The methylene chloride extract was dried over Na_2SO_4 , after which the product was isolated by precipitation with excess pentane. The signals assigned to the two inequivalent olefinic
20 protons on the starting synthon had disappeared indicating complete oligomerization of the synthon anion.

Example 4

25 In 10 mls of tetrahydrofuran (THF) containing 1.3 g of Mg metal shavings (pretreated with 1,2 dibromoethane to clean surface) 2 g of 2-4-bromostyrene was added dropwise at 50°C under rapid stirring. The formation of the Grignard reagent proceeded quickly to
30 form a light amber solution. The solution was filtered to remove the excess Mg metal. Thereafter, 7.8 g of tripentafluorophenylboron in 25 mls THF was added to the Grignard reagent at room temperature. The mixture was stirred for 10 minutes at room temperature before
35 pentane (50 ml) was added to precipitate a white ionic solid. The solid was collected by filtration, washed with pure pentane and dried in vacuum. The ^1H and ^{13}C

NMR spectra of the solid in d_8 -THF confirmed the structure to be the THF adduct of the magnesium bromide salt of the styrene (Sty) modified synthon: $[\text{MgBr} \cdot \text{THF}_x]^+[(\text{pfp})_3\text{BSty}]^-$.

5

Example 5

2.0 g of the styrene modified synthon prepared in Example 4 was dissolved in 50 mls of methylene chloride. The methylene chloride layer was treated with 10 0.3 grams of dimethylanilinium hydrochloride. The resulting mixture was washed three times with 50 mls of water to remove the magnesium halide biproduct. The methylene chloride layer was dried using Na_2SO_4 , filtered. The product was crystallized from methylene 15 chloride concentrates at low temperature to yield 0.7 grams of a thermally unstable white solid. The initially isolated material was characterized to be $[\text{DMAH}]^+[(\text{pfp})_3\text{BSty}]^-$. Thermal decomposition via cationic mechanisms led to the oligomerization of the 20 target synthon over 12 hours at room temperature. The isolated synthon and its thermal decomposition products were reacted with Cp_2HfMe_2 and formed active olefin polymerization catalysts.

25 Example 6

3.43 g of the product prepared in Example 4 was dissolved in 15 mls of methylene chloride and treated with 0.85 g of $\text{Et}_4\text{N}^+\text{Cl}^-$. Excess 1,4 dioxane was added to precipitate the magnesium halide. The insolubles 30 were removed by filtration, and the resulting methylene chloride solution of the crude product was washed three times with water, dried over Na_2SO_4 , and was crystallized by addition of Et_2O . The resulting thermally stable crystalline product was found to have 35 the composition, $[\text{Et}_4\text{N}]^+[(\text{pfp})_3\text{BSty}]^-$, by high field NMR spectroscopy.

Example 7

0.26 grams of DVB (a mixture of divinylbenzene isomers) was dissolved in 50 mls of pentane. 1.5 mls of 1.3M s-BuLi was added to the stirred solution causing an immediate color change from clear to orange. After 5 minutes a orange polymeric solid precipitate had formed and 1 g of tripentafluoro-phenylboron was added causing formation of a lightly color solid precipitate. The solvent was reduced by 30% and 0.28 grams of [DMAH][Cl] in 50 mls of methylene chloride was added. A white precipitate is formed. The precipitate was removed by filtration. The soluble portion was concentrated and titrated with excess pentane to precipitate a white polyionic solid. The solid was isolated by filtration, extracted with methylene chloride, filtered, and reprecipitated with pentane to give a low molecular weight polyionic activator: $[\text{DMAH}^+]_n [((\text{pfp})_3\text{B})_n\text{-PDVB}]^{n-}$ (where PDVB represents a polydivinylbenzene oligomeric core T).

Example 8

5 grams of paramethylstyrene (PMS) and 0.5 g of DVB were diluted in 100 mls of pentane and stirred while 3.6 mls of a 1.09M solution of s-BuLi was added. The formation of a red gel began to form indicating the formation of the desired living crosslinked poly-PMS core T". The pentane was removed in vacuum and 3.97 grams of $\text{B}(\text{pfp})_3$ in 50 mls of toluene was added. The mixture was stirred for 3 hours before the red color had disappeared leaving an off-white gel/toluene mixture. The solvent was removed in vacuum and 0.56 grams of [DMAH][Cl] in 100 mls of methylene chloride was added. The mixture was stirred 12 hours, filtered. The solid was washed 3 times with 20 mls of methylene chloride, and dried in vacuum to give 4.8 grams of a crosslinked polystyrene supported polyionic activator:

$[\text{DMAH}^+]_n [((\text{pfp})_3\text{B})_n\text{-XPMS}]^{n-}$ (where XPMS represents the crosslinked polyparamethylstyrene core T).

Example 9

5 Bulk propylene (400mls) was polymerized in a stainless steel autoclave at 40C using a catalyst prepared by the combination of 0.022 g of
10 rac-Me₂Si(H₄-Indenyl)ZrMe₂ and 0.007 g of the norbornylene functionalized synthon prepared in Example 2. The reactor temperature increased to 42C during the 30 minute polymerization. The unreacted propylene was vented and 28 grams of isotactic polypropylene was isolated. GPC established that the polymer had a weight average molecular weight of 17K and a molecular
15 weight distribution of 2.4.

Example 10

Bulk propylene (400mls) was polymerized in a stainless steel autoclave at 40C using a catalyst
20 prepared by the combination of 0.018 g of rac-Me₂Si(H₄-Indenyl)ZrMe₂ and 0.006 g of the polynorbornylene polyionic activator prepared in Example 3. The reactor temperature increased to 45C during the 5 minute polymerization. The unreacted
25 propylene was vented and 38 grams of isotactic polypropylene was isolated. GPC established that the polymer had a weight average molecular weight of 20K and a molecular weight distribution of 2.6.

Example 11

30 Bulk propylene (400mls) was polymerized in a stainless steel autoclave at 40C using a catalyst prepared by the combination of 0.019 g of rac-Me₂Si(H₄-Indenyl)ZrMe₂ and 0.006 g of the DVB polyionic activator prepared in Example 7. The reactor
35 temperature was held at 40C during the 30 minute polymerization. The unreacted propylene was vented and

4.1 grams of isotactic polypropylene was isolated. GPC established that the polymer had a weight average molecular weight of 10K and a molecular weight distribution of 2.5.

5

Example 12

Bulk propylene (400mls) was polymerized in a stainless steel autoclave at 40C using a catalyst prepared by the combination of 0.10 g of
10 $\text{rac-Me}_2\text{Si}(\text{H}_4\text{-Indenyl})\text{ZrMe}_2$ and 0.10 g of the Styrene-DVB polyionic activator prepared in Example 8. The reactor temperature increased to 48C during the 30 minute polymerization. The unreacted propylene was vented and 150 grams of granular isotactic
15 polypropylene was isolated. GPC established that the polymer had a weight average molecular weight of 23K and a molecular weight distribution of 2.2.

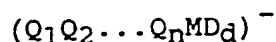
Although the invention has been described with reference to its preferred embodiments those skilled in
20 the art may appreciate changes and modification thereto which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

CLAIMS

1. A polyanionic moiety comprising a plurality of metal or metalloid atom - containing, non
5 coordinating anionic groups pendant from and chemically bonded to a core component.

2. A polyanionic moiety according to claim 1 wherein the anionic groups comprise a metal or
10 metalloid element chemically bonded to the core component via a bridging moiety.

3. A polyanionic moiety according to claim 1 or 2 wherein the anionic groups are represented by the
15 formula



wherein:

20

M is a metal or metalloid element selected from Groups 3-15;

25 $Q_1 - Q_n$ are radical ligands each of which is, independently, hydride, halide, disubstituted amido, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or a hydrocarbyl-or halocarbyl-substituted organometalloid;

n is the number of Q-ligands;

d is 0 or 1; and

30 when d is 1, D is a bridging moiety which links a pendant non-coordinating anion to the core.

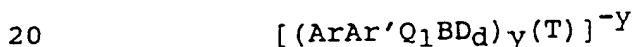
4. A polyanionic moiety according to claim 2 or 3 wherein the bridging moiety is a hydrocarbyl, halocarbyl, substituted hydrocarbyl, hydrocarbyloxy, aryloxy, oxo, imido, or sulfido group.
35

5. A polyanionic moiety according to any one of the preceding claims wherein the non coordinating anionic groups comprise radical ligands bonded to the metal or metalloid element, at least one of said radical ligands being an aromatic or substituted aromatic radical containing from 6 - 20 carbon atoms.

6. A polyanionic moiety according to claim 5 wherein at least one, preferably each, radical ligand is a pentafluorophenyl group.

7. A polyanionic moiety according to any one of the preceding claims wherein the metal or metalloid is an element of Group 4, 5 or 13 of the Periodic Table of the Elements, preferably boron or aluminum.

8. A polyanionic moiety according to claim 7 represented by the formula



wherein

Ar and Ar' are the same or different aromatic or substituted aromatic hydrocarbyl radical containing from 6 to 20 carbon atoms;

T is the core component;

B is boron;

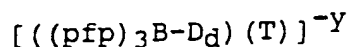
d is 0 or 1;

when d is 1, D is a bridging moiety which chemically links the boron atoms to the core T;

Q₁ is a halide, hydride, hydrocarbyl or substituted hydrocarbyl radical containing from 1 to 20 carbon atoms, or an aromatic or substituted aromatic radical containing at least 6 carbon atoms; and

y is an integer equal to or greater than 2.

9. A polyanionic moiety according to claim 8 represented by the formula

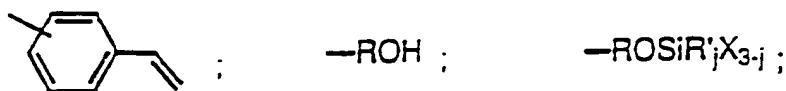


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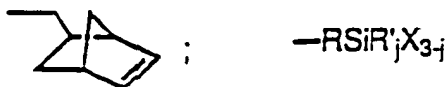
wherein pfp is pentafluorophenyl

10. A polyanionic moiety according to any one of the preceding claims when derived from an intermediate compound in which the metal or metalloid element of the non coordinating anionic groups is chemically bonded to a reactive radical containing at least one reactive functional group, said radical being chemically reactable with the core component, or being polymerizable with other such intermediate compounds and optionally other comonomer to form the core component.

11. A polyanionic moiety according to claim 10 wherein the reactive radical comprises



25



30 wherein each R is independently a hydrocarbyldiradical, X is a halide or alkoxide radical and j is 0, 1 or 2.

35 12. A polyanionic moiety according to any one of claims 1-9 wherein the core component comprises a cross-linked polystyrene or polydivinyl benzene

polymeric core, or a polyanionic Lewis basic core substrate reactable with a Lewis acid.

13. A polyanionic activator composition
5 comprising a polyanionic moiety according to any one of the preceding claims and a plurality of cations Ct which balance the charge of the non-coordinating anionic groups.

10 14. A polyanionic activator composition according to claim 13 wherein the cations Ct are reactive with a leaving group ligand of a ligand stabilized transition metal compound.

15 15. A polyanionic activator composition according to claim 14 wherein the cations Ct are ammonium, phosphonium, carbonium, oxonium, tropylium or silver cations or are represented by the formula

20 $[LH]^+$

wherein

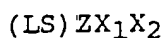
L is a neutral Lewis base and $[LH]^+$ is a Bronsted acid.

25 16. A polyanionic activator composition according to claim 15 wherein L is ammonia, an amine or hydrocarbyl substituted amine, or aniline or a N-hydrocarbyl substituted aniline.

30 17. An activated catalyst composition comprising a polyanionic moiety according to any one of claims 1-12, a plurality of the pendant non coordinating anionic groups of which are in non-coordinating association
35 with a plurality of cationic transition metal components derived from one or more ligand stabilized transition metal compounds.

18. An activated catalyst composition according to claim 17 which comprises a product of reaction between (i) a transition metal compound having at least one leaving group ligand, for example a ligand which is hydrolyzable with water, and (ii) a polyanionic activator-composition according to claim 14, 15 or 16.

19. An activated catalyst composition according to claim 17 or 18 wherein the transition metal compound is of the formula



wherein

Z is a group 3 to 10 transition metal, X_1 is an anionic leaving group ligand or a non-coordinating anion leaving group, X_2 is a hydride or hydrocarbyl ligand, and (LS) is a ligand system which completes the coordination number of Z.

20. An activated catalyst composition according to claim 17, 18 or 19 wherein the transition metal compound has a ligand system coordinated to the transition metal, which system comprises (i) two cyclopentadienyl ligands, each optionally substituted and the two optionally being bridged with a bridging atom or group or (ii) a single, optionally substituted, cyclopentadienyl ligand and a heteroatom - containing ligand, the two ligands optionally being bridged with a bridging atom or group.

21. A method of producing an activated catalyst composition according to any one of claims 17 - 20 which comprises contacting (i) a transition metal compound having at least one leaving group ligand, for example a ligand which is hydrolyzable with water, and

(ii) a polyanionic activator composition according to any one of claims 13 - 16 for a time and under conditions sufficient to allow cations of (ii) to react with the leaving group ligands of (i).

5

22. A method of producing an activated catalyst composition according to any one of claims 17 - 20 which comprises contacting (i) a transition metal composition comprising a transition metal cationic component stabilized with a single non-coordinating anionic component with (ii) a polyanionic activator composition according to any one of claims 13 - 16 for a time and under conditions sufficient to allow (a) cations of (ii) to react with the non coordinating anionic component of (i), and (b) the transition metal cationic components of (i) to form a stable non-coordinating association with the polyanionic moiety of the polyanionic activator composition.

23. A process for polymerizing an olefin to a polyolefin which comprises contacting an olefin monomer and optionally one or more comonomers with an activated catalyst composition according to any one of claims 17 - 20 or produced by the method according to claim 21 or 22, at a temperature and for a time sufficient to polymerize at least a portion of the olefin to a polyolefin.

24. A process according to claim 23 wherein the polyanionic moiety of the activated catalyst composition is insoluble in the monomer.

25. A process according to claim 24 wherein the activated catalyst composition is immobilized with regard to a fluidized flow of monomer or polymer, which process comprises maintaining monomer in fluidized contact with the immobilized activated catalyst

composition at a temperature and for a time sufficient to polymerize at least a portion of the olefin to a polyolefin, and removing the polyolefin from contact with the activated catalyst composition.

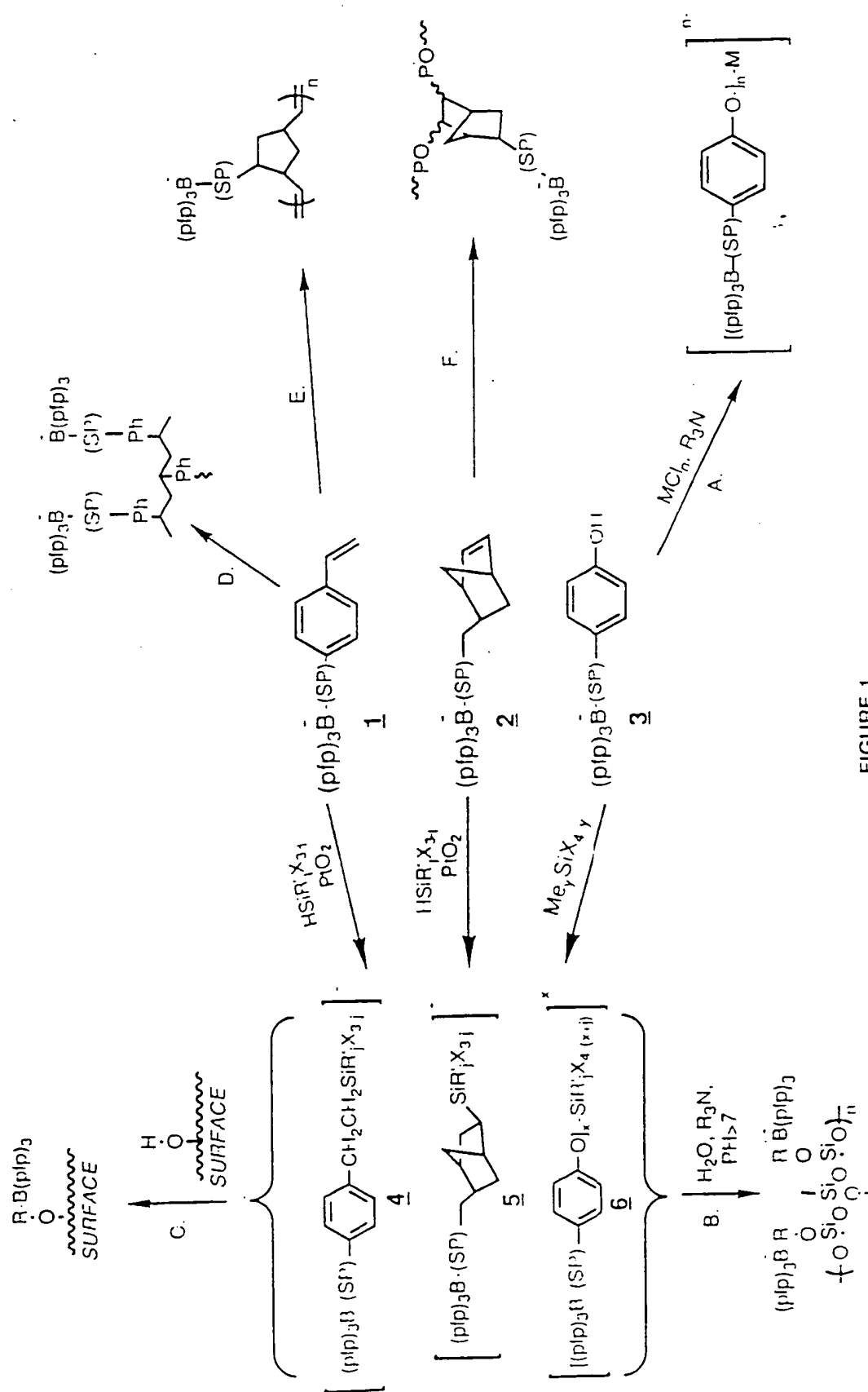


FIGURE 1

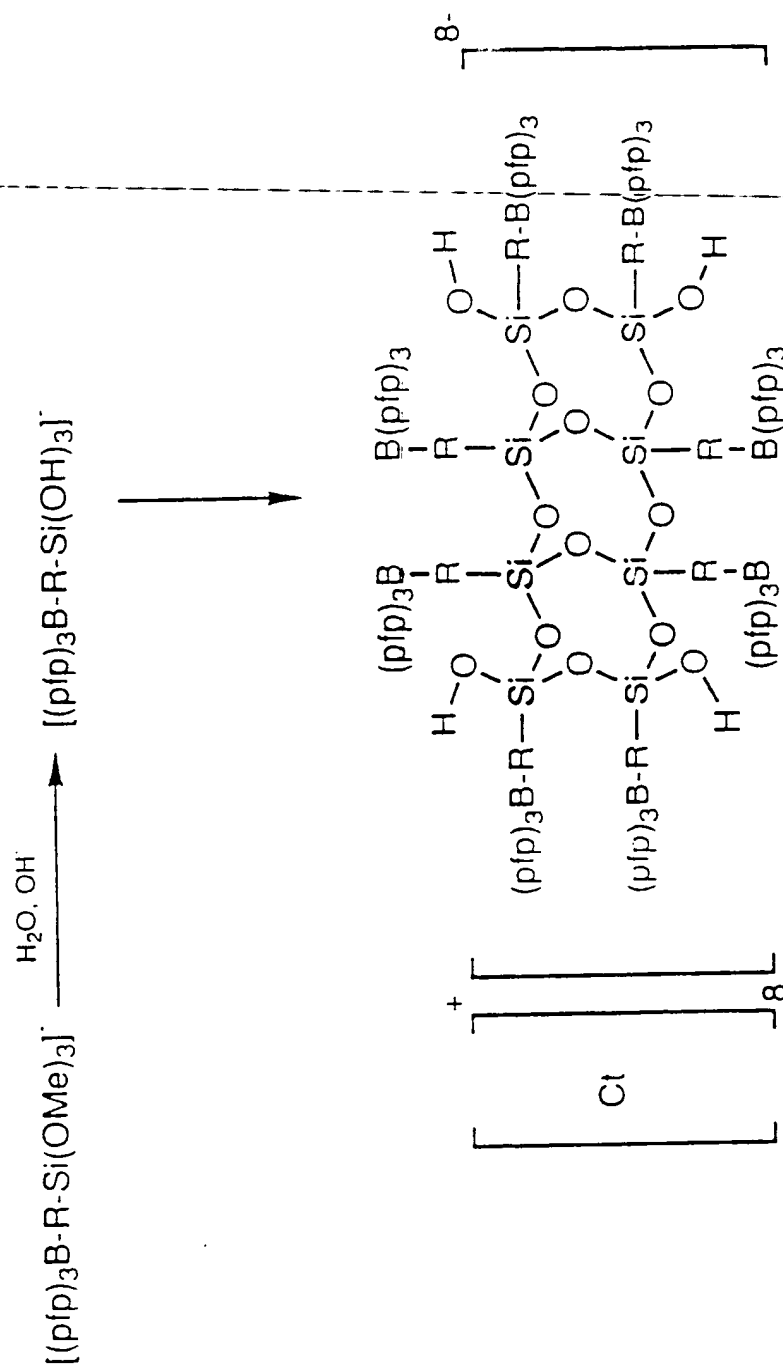


FIGURE 2

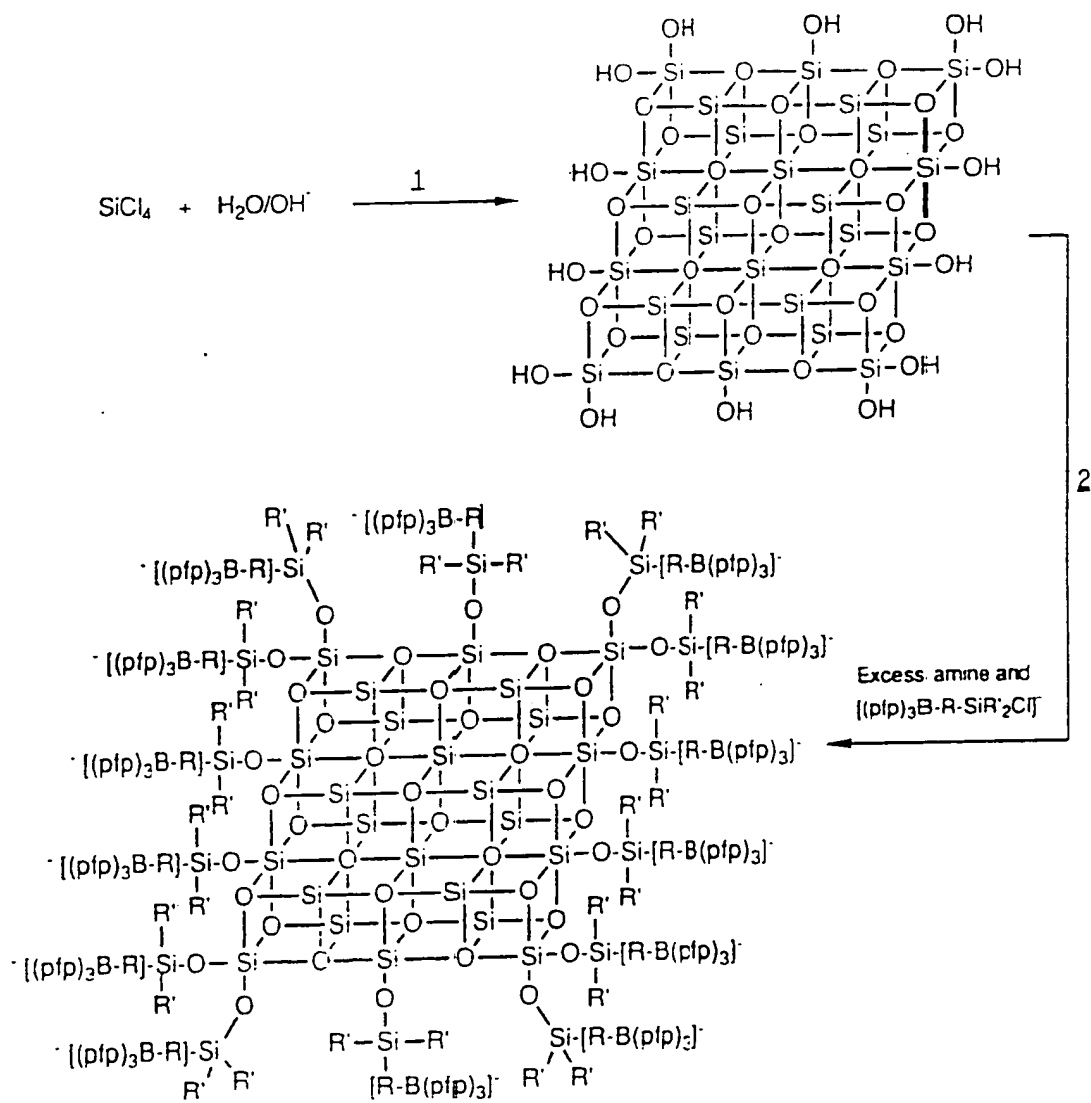


FIGURE 3

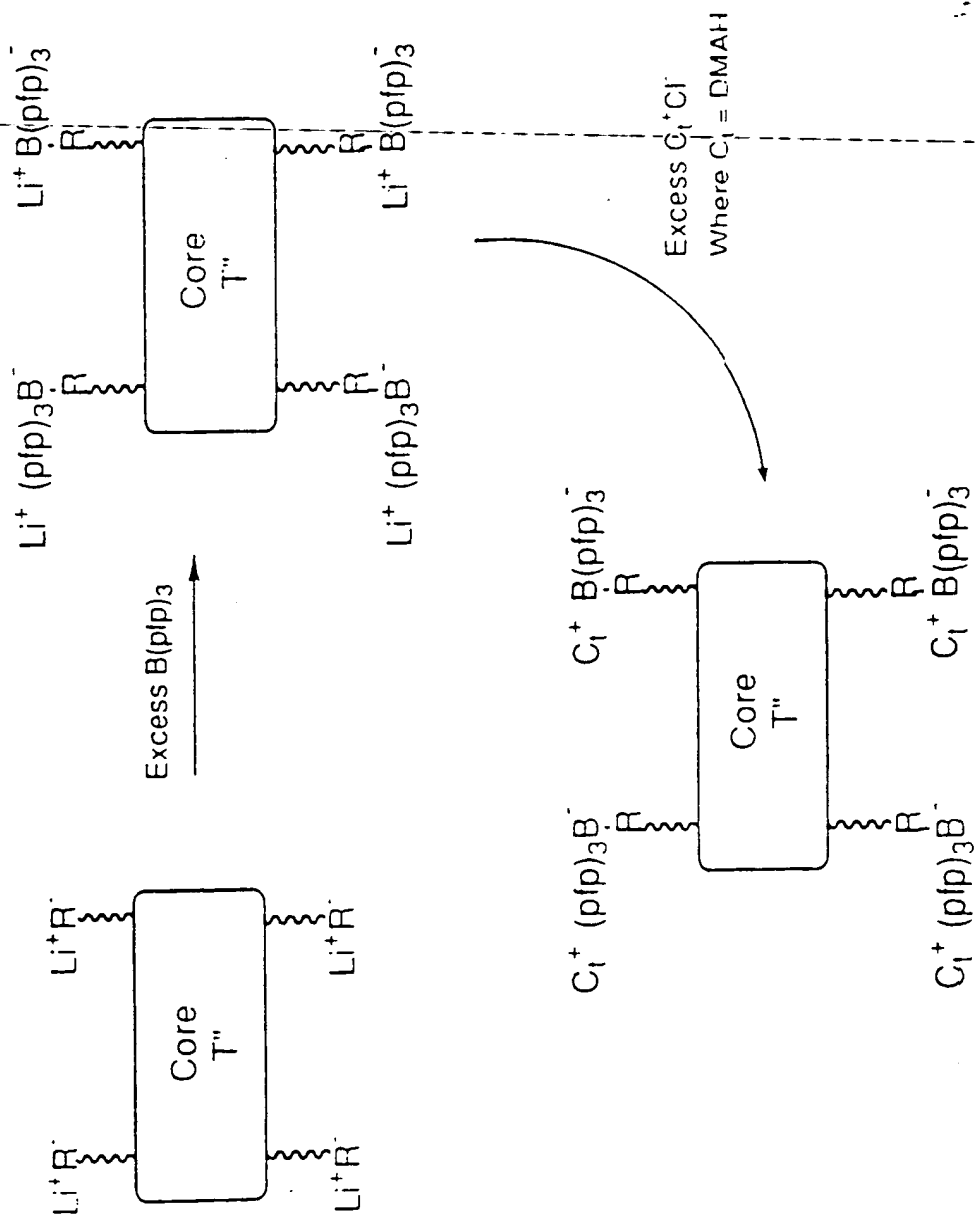


FIGURE 4

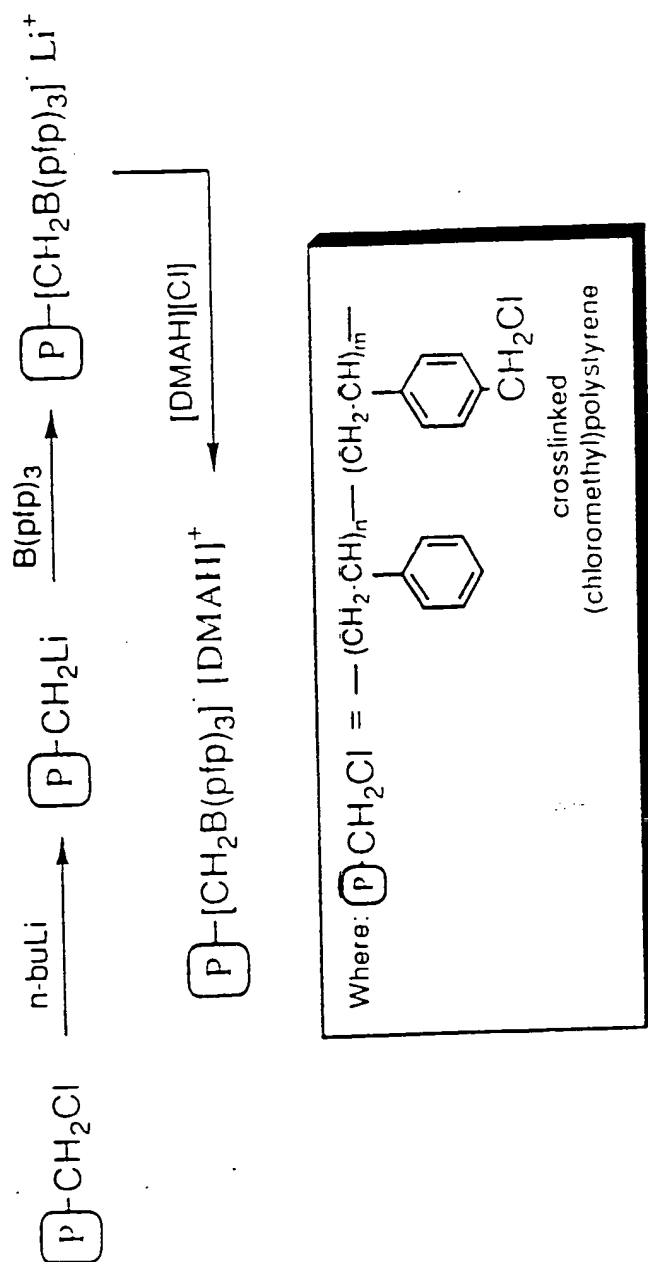


FIGURE 5

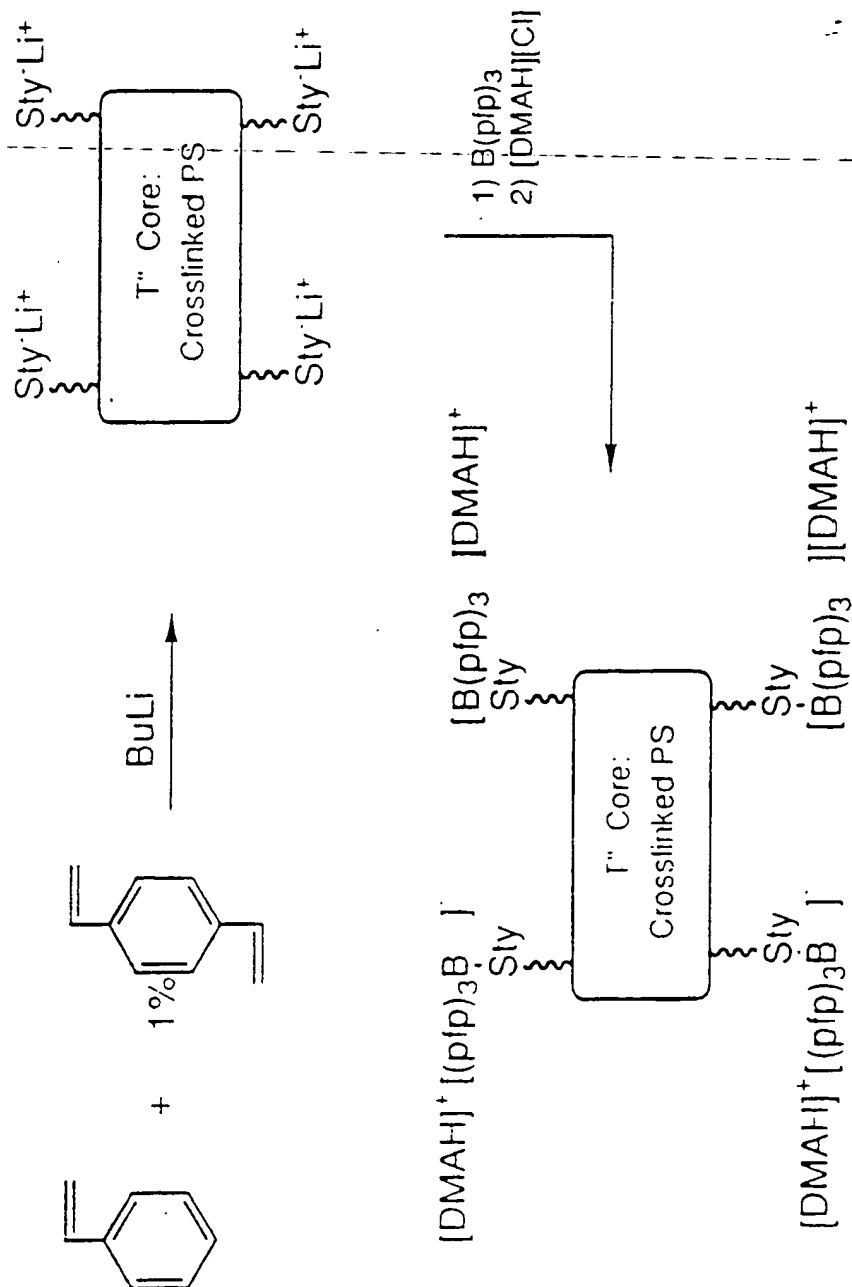


FIGURE 6

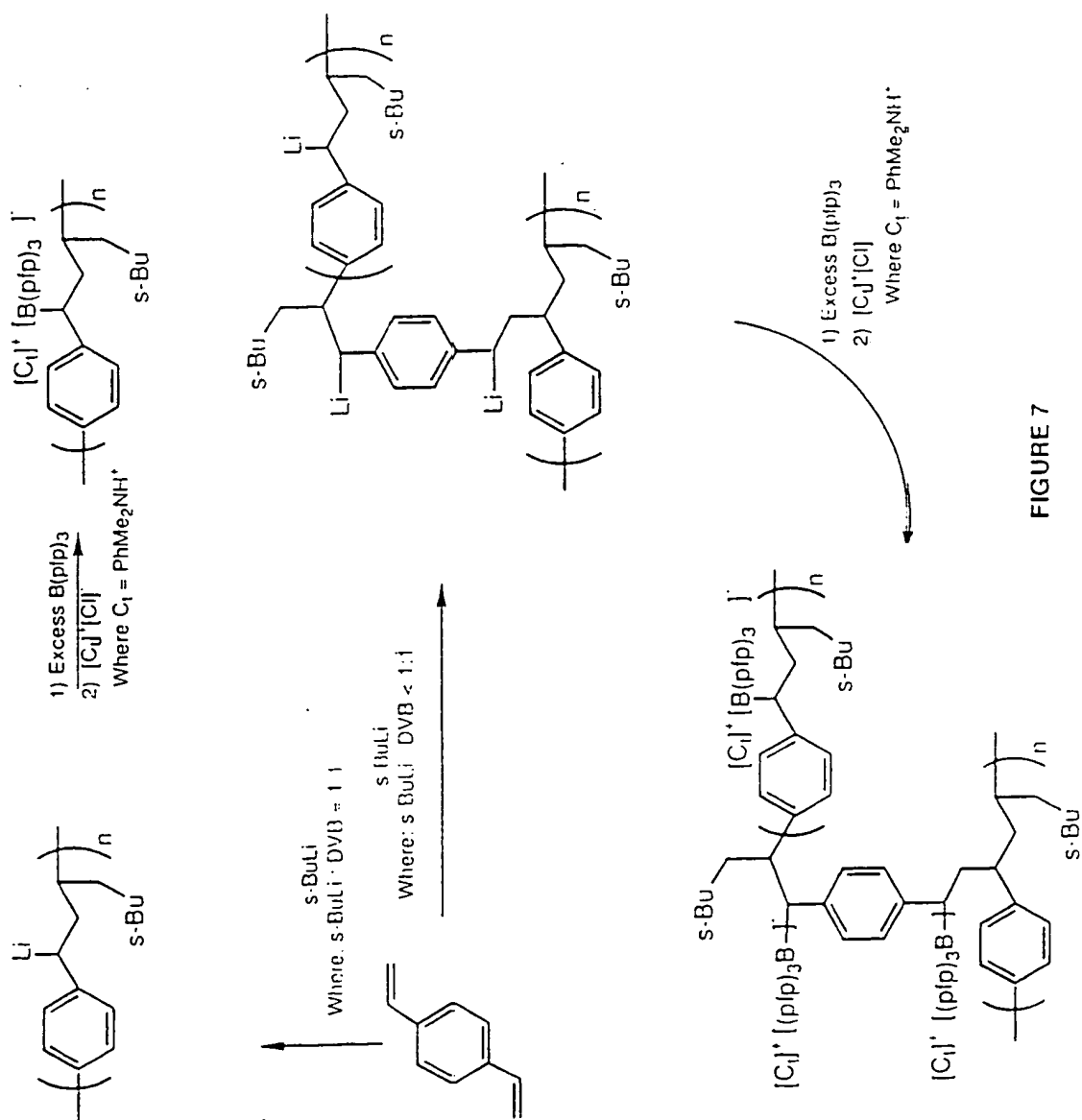


FIGURE 7

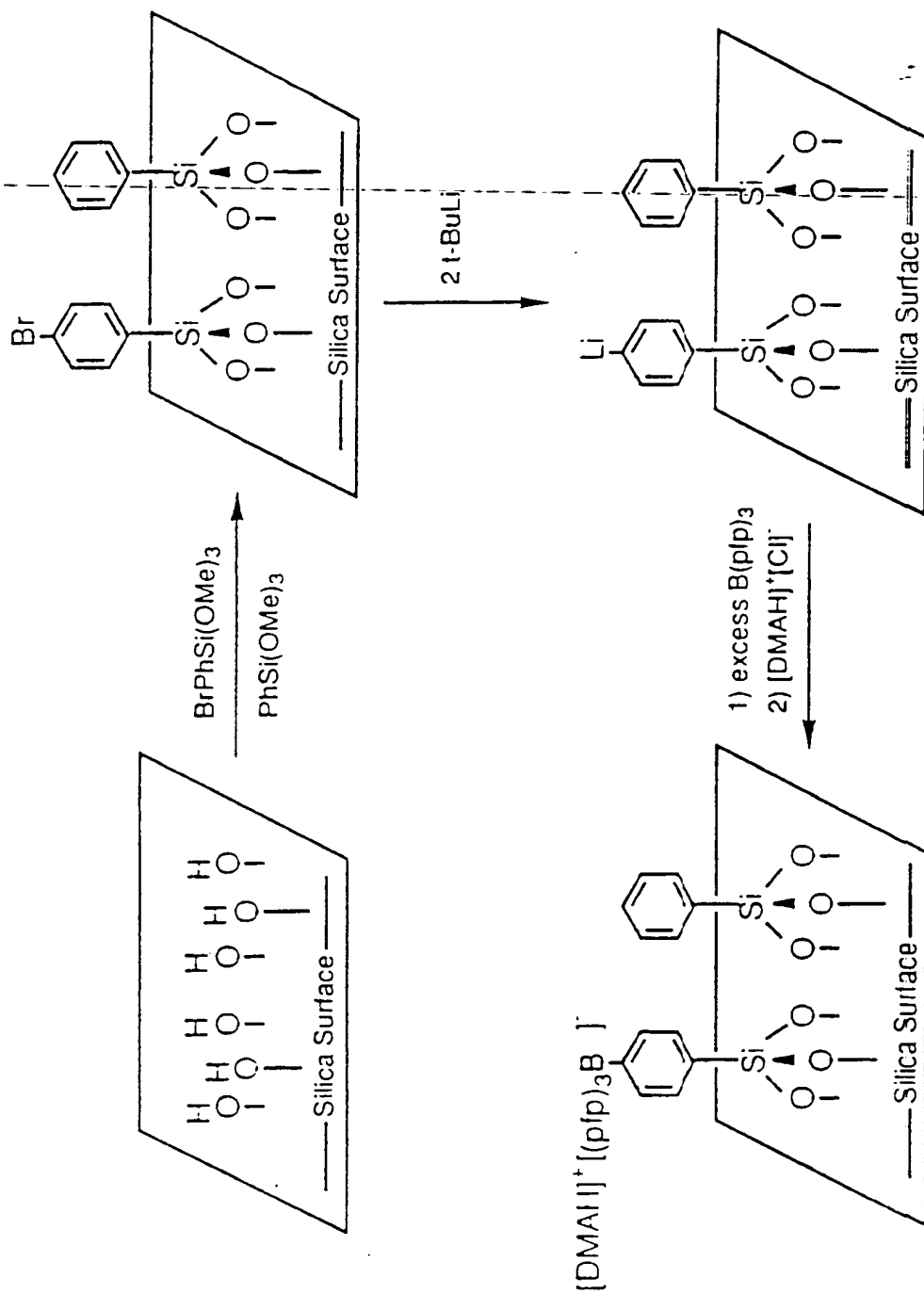


FIGURE 8

INTERNATIONAL SEARCH REPORT

PCT/US 92/10296

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F10/00; C08F30/06; C09C1/30		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F ; C09C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 230 247 (KANEGAFUCHI KAGAKU KOGYO KABUSHIKI KAISHA) 29 July 1987 see claims 1,4,9 see page 3, line 1 - line 5 see page 3, line 47 - page 4, line 49 ---	1,3
X	EP,A,0 163 214 (PPG INDUSTRIES) 4 December 1985 see claims 1,24 see abstract see page 5, line 5 - line 17 see page 6, line 2 - line 4 see page 8, line 25 - page 9, line 4 ---	1
A	EP,A,0 293 815 (HOECHST AKTIENGESELLSCHAFT) 7 December 1988 see the whole document ---	-/--
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"d" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
12 MARCH 1993	07.04.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FISCHER B.R.	

Form PCT/ISA/210 (extra sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210296
SA 67685

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 12/03/93

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